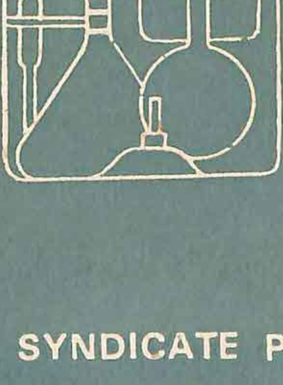
S. N. Poddar
and
J. Haldar

# Higher Secondary Practical Chemistry



BOOK SYNDICATE PRIVATE LTD.

9870
SW

# HIGHER SECONDARY
# PRACTICAL CHEMISTRY

[Includes West Bengal Syllabus
AND
Gauhati & Tripura Syllabuses]

STATE INSTITUTE OF EDUCATION
Govt. of West Bengal

By

**Dr. SAILENDRA NATH PODDAR, M. SC., PH. D., D. SC.**
Professor, Inorganic Chemistry Department,
Indian Association for the Cultivation of Science, Calcutta.
Author : Higher Secondary Chemistry—Vol. I & II (Ordinary level course) and Vol. III (Advanced level course).

AND

**Dr. JAGABANDHU HALDAR, M. SC. PH. D.**
Lecturer, Chemistry Department, Seth Anandram
Jaipuria College, Calcutta.
Author : Higher Secondary Chemistry Vol. I & II (Ordinary level course) and Vol. III (Advanced level course).

BOOK SYNDICATE PRIVATE LIMITED
2, RAMNATH BISWAS LANE, CALCUTTA-700009

First Edition : 1976
Second Edition : 1978
Third Edition : 1980

*To*
*Shanti*

© *COPYRIGHT RESERVED*

9870

**Price : Rupees Seven and paise fifty only.**

Paper used for printing the book was made available by the Titaghur Paper Mills Co. Ltd. Calcutta, @ Rs. 4,600 Per Ton (Ex-Mill Price).

---

Published by Sree Kripasindhu Das, M. A. B. T.
For Book Syndicate (P.) Ltd. 2, Ramnath Biswas Lane,
Calcutta-9 and Printed by Sri Pradipkumar Hazra at
Sreemudran, 40, Shibnarayan Das Lane, Calcutta-6.

## WEST BENGAL SYLLABUS
## PRACTICAL CHEMISTRY

[ *General Stream Course* ] Full Marks—40

In order to ensure that the students carry out all the experiments mentioned in the Syllabus, a number of sets of questions should be set in the examination, covering all experiments. One common set of questions should not be given to all examinees. Each examinee should draw one set of questions from a number of such sets during the examination.

Each set will contain two questions, **one from Group A of experiments carrying 20 marks and the other from Group B of experiments carrying 10 marks.**

5 marks are allocated for neat performance of the experiments in the examination and 5 marks for Laboratory Note Book.

**Group A of experiments :—**

Experiments Nos. 6, 8, 9, 10.

**Group B of Experiments :—**

Rest of the experiments in the Syllabus,

1. An experiment to illustrate scientific method—Experiment, Observation and Conclusion, such as Black-box experiment. (A solid enclosed in a completely closed wooden box, 15 cm. × 15 cm. × 10 cm.—To find out the nature of the solid—light, heavy, circular. cylindrical, round, platy, or of irregular shape etc.

2. Study of the Bunsen burner and its flame or study of a candle flame.

3. Fitting up of a wash bottle.

4. Separation of mixtures by filtration, sublimation ; Preparation of distilled water from salt-water.

5. Crystallisation of Copper sulphate or any other suitable salt and collection of the crystals. Separation of NaCl from a solution of NaCl and $NaNO_3$, or NaCl and $MgSO_4$ by fractional crystallisation.

6. Preparation of $CO_2$, $H_2S$, $NH_3$ and HCl—and study of their properties : Collection of $CO_2$ by water-displacement and of $NH_3$, HCl, $H_2S$ by air-displacement.

7. Study of the chemical balance and of the weight box—method of weighing (Actual weighing of a sample by each student is necessary).

8. Equivalent weight of magnesium or aluminium or zinc by hydrogen displacement method. (Weighed sample of the metal should be given to the student.)

9. Acidimetry and alkalimetry :

(*a*) Determination of the strength of

(i) an unknown $H_2SO_4$ solution,

(ii) an unknown NaOH solution, using both methyl orange and phenolphthalein as indicator.

10. (*a*) Dry and Wet tests of the following radicals :

$Pb^{++}$, $Cu^{++}$, $Fe^{++}$, $Fe^{+++}$, $Al^{+++}$, $Zn^{++}$, $Ca^{++}$, $Mg^{++}$.

(*b*) Detection of two of the above radicals in an unknown mixture containing only two such radicals by dry and wet tests. (Solid mixture supplied should be soluble in water or dil. HCl.)

11. (*a*) Tests of the the following acid radicals :

$CO_3^{=}$, $Cl^-$, $S^{=}$, $SO_4^{=}$ and $NO_3^-$.

(*b*) Detection of one acid radical in a single unknown solid salt.

[ *Vocational Stream Course* ] (Marks—20)

1 to 3.—Same as *General stream course.*

4. Separation of a mixture of common salt and sand by the process of solution, filtration and evaporation to form a concentrated solution and cystallisation of the common salt.

5. Preparation of cabon dioxide gas and ammonia gas and study of their important properties.

6. Same as *General stream course. no. 7.*

7. (*a*) Dry and wet tests of the following radicals :

$Cu^{++}$, $Fe^{++}$, $Fe^{+++}$, $Zn^{++}$; $Ca^{++}$, $Mg^{++}$.

(*b*) Detection of one of the above radicals in an unknown solid sample containing only one such radical (the solid sample supplied should be soluble in water or dilute HCl).

# CONTENTS

*Chapter* *Page*

Introduction .... i

Black-box Experiment ... iii

Practical Chemistry ... vi

General Instructions ... vii

Accidents and Remedies .... x

Apparatus commonly used in the laboratory ... xi

1. Study of Bunsen burner and its flame ... 1

2. Fitting and handling of apparatus : Fitting up of a wash bottle .... 12

3. Separation of mixtures by common laboratory processes. .... 20
Crystallisation of copper sulphate from water (29), Separation of sodium chloride from sodium nitrate (31), Separation of sodium chloride from magnesium sulphate (31).

4. Preparation of gases and studies of their ... 34
properties : Hydrogen* (34), Oxygen* (38), Carbon dioxide (43), Ammonia (47), Sulphuretted hydrogen (53), Hydrogen chloride (59).

5. Study of the chemical balance and weighing of substances. ... 66

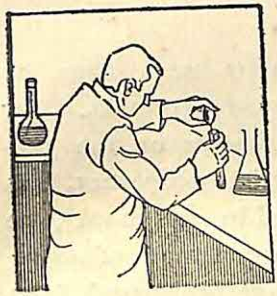
6. Determination of equivalent weight of metal. ... 78

7. Volumetric analysis—Acidimetry and Alkalimetry. ... 84

8. Qualitative inorganic analysis— ... 111
Dry tests of basic radicals (115), Ignition test (116), Charcoal block test (118), Flame test (120), Borax bead test (122), Wet tests for individual basic radicals (125). Preparation of solution (126). Reactions of : Lead ion (127), Copper ion (129), Ferrous ion (130), Ferric ion (133), Aluminium ion (136), Zinc ion (137),

Calcium ion (140). Magnesium ion (141).
Tests for acid radicals ... 143
Carbonate (143), Chloride (146), *Bromide (150), *Iodide (151), Nitrate (153), *Nitrite (156), Sulphide (158), Sulphate (159).
Systematic Preliminary Tests for Acid Radicals 161
Systematic Wet Tests for Basic Radicals ... 164
Model Analysis of unknown Salts ... 173

[N. B. *Subject-matters marked with asterisk (*) in the text are not included in W. B. Syllabus.*]



# INTRODUCTION

**Scientific Conception needs Experimentations.**

Basically, science is a manner of thinking with reasoning to unveil the cause of the observed effects or the effects of the cause. Thus, it implies that, to have scientific conception of, and to make a definite statement regarding phenomenon, one has to proceed carefully through a number of steps consisting of the performance of a series of experiments with correct observations, collections of facts therefrom, methodical correlation among the observed facts and finally, the formulation of a generalised principle. All these collectively comprise what is known as the scientific method of study.

Scientific laboratories are the places where the scientists are engaged in finding out new ways and devising new methods of experiments to solve certain problems and thereby unveil the cause of some natural phenomena. When the same effects are required to be reproduced, the experiments are required in exactly the same way. For these reasons, laboratories of schools and colleges, and also other scientific laboratories where pupils are taught science and are offered training on various scientific methods and operations, are equipped with all the necessary apparatus and instruments. It is the duty on the part of the pupils to perform the experiments carefully and thereby make clear and deep-rooted conception of the scientific phenomana they are taught.

It is an accepted fact that, it is much easier to give an idea of what *light* is, by igniting a match-stick in a dark room than by saying hundreds of words to the students on the subject. Similarily, a student will understand and remember the properties (chemical or physical) of a substance more easily and clearly by observing the changes it undergoes on heating or dissolving or under the action of certain reagents, than by committing them to memory from theoretical text-books. For example, if a student performs the experiments on the preparation of ammonia gas and studies of its properties, as included in the syllabus (and described in this book), he need not commit to memory the 'laboratory method of preparation of $NH_3$, its drying and its important properties' from the theoretical text-books, for he will vividly remember what he has done with his own hands in this regard in his practical classes. Here lies the importance and usefulness of *practical chemistry* course. Further, in their future lives, some students may come out as analysts, research chemists or production chemists in any institute or organisation, where they will have to carry out experiments, or analyse with their own hands. This preliminary training in practical chemistry at this level (which will be elaborated more and more in subsequent advanced studies of the subject) will then be of much help to them While working in practical classes, students will be gradually coversant with the possible difficulties and drawbacks in certain experiments and learn how to overcome them and obtain better results. Above all, the performance of a chemical experiment helps the student cultivate and develop his power of observation and helps him draw probable inferences from what he has observed. This also produces an inquisitiveness in the mind of the student as to what would happen if the experiment is done in some other way, or what would happen if some other *reagent* was used instead of the one prescribed and *so on.* And this inquisitiveness is the *mother of all inventions.*

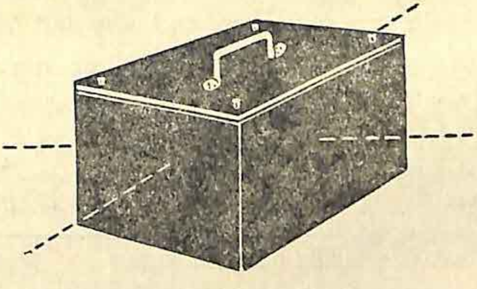
**The Correct Inference—The Most Important Thing :**

In a scientific experiment (especially the chemical experiments) a correct inference is to be drawn from the facts observed in the experiment. Suppose in a chemical experiment, we add some *reagent* to a solution of a substance, when a precipitate is formed or a colour is produced or a gas is evolved. We only observe some outward manifestation of what has happened *chemically*. From this outward manifestation, we are to *logically* correlate phenomena and *build* up the most probable chemical reactions that might have taken place within the system, and from all these, we are to draw the *inference*. This, of course, requires some clear understanding of the fundamentals of the chemistry proper, and students are to develop this faculty gradually.

A very illustrative example may be cited regarding the usefulness of correct logical inferences in the scientific study. We have not and cannot see atoms or molecules or ions. But, by studying some of their characteristic properties and some physical (or chemical) phenomena, we have been successful in ascertaining with a fair degree of accuracy, their nature, size, shape, charge, modes of undergoing changes etc.

Thus, correct inferences are of utmost importance in deciding the nature and identity of an unknown thing. The ability to make correct inferences from observed results requires experience, and students are to develop this power, first through experiments with known substances and then with an unknown substance. An interesting piece of experiment to infer about the physical state shape and size (or weight of an unseen solid substance is the **Black Box Experiment** which is described below :

**Black Box Experiment :** A rectangular box made of plywood (about 1 cm. thick), measuring 15 cm. × 15 cm. × 10 cm. and provided with a lid of the same material is taken The lid can be closed by screws or nails. The outside of the box is painted black. Several such boxes may be prepared, and in each is placed a solid object of a particular shape, size and weight, and the lid is closed by screws or nails It is necessary that the students should not see the objects which have been placed inside the boxes, before they have carried out the experiments and drawn thir inferences therefrom. If necessary, the boxes may be opened after the experiments are done, and the results or *findings* submitted by the students may be verified in order to show them how far their inferences tallied with the actuality. Each student should be allowed to experiment with *all* the boxes so prepared in order that he can gather



The Black Box

sufficient experience by repeated trials and *observations* to come as much close to the correct *Inferences* as possible.

Any *rational* procedure may be adopted by the students to obtain any *clue* regarding the nature of the object enclosed in the box. But, the particular experiment must be well thought-of and the students should first ask themselves why they want to do a particular experiment and what results they expect from it, or what *inferences* they propose to draw from any particular *observation* from that experiment. The point which is proposed to be stressed upon is that, no experiment should be done aimlessly, because there is little chance to come to a correct conclusion from an aimless experiment. This is to be always borne in mind that scientific methods are no magic ; there is always a *cause* of an observed *effect* or the *effect* of an observed *cause*. The correlation of these two factors is the life of scientific method of study.

A few possible procedures which may help to draw correct *inferences* regarding the solid object enclosed in the box are given below in a tabular form. The students may try to innovate some more well-thought-of experiments to achieve their ends and present their results in a tabular form and thus draw their own conclusions from the results of the experiments.

The box is a rectangular one and we will tilt and rotate the box about its three axes separately and note and *feel* the sound produced by the object inside the box. For starting an experiment, the box is tilted to bring the object at one side of the box, which is then kept in a horizontal position.

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. The box is tilted along its length-wise axis slightly. | The object inside the box *rolls* and strikes the opposite wall of the box. | The object may be *spherical* or *cylindrical*. |
| 2. The box is tilted slightly along its breadth-wise axis. | (*a*) The object inside the box *rolls* similarly as in expt. (1). | The object is most probably *spherical*. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
|  | (*b*) The object inside the box does not roll, but it *slides* across the floor of the box and strikes the opposite wall. | The object is most probably *cylindrical*. |
| 3. The box is rotated by giving a slight whirling motion in a horizontal plane about its vertical axis. | The object inside the box *rotate* easily and freely in tune with the whirling motion of the box. | The object is most probably *spherical*. |
| 4. (*a*) The box is tilted along its lengthwise-axis only slightly. | Nothing particular happens. | No inference. |
| (*b*) The box is tilted more along the above axis. | The object inside the box *slides down* along the floor of the box with a uniform sound and strikes the opposite wall of the box. | The object has probably a *plane* surface. |
| (*c*) The box is turned upside-down and experiment similar to (*b*) is performed. | Same observation as above. | The object has probably two opposite surfaces *plane*, or it is probably *platy*. |
| (5) Experiment similar to 4 (*b*) is performed. | The object inside the box slides down with an *erratic rattling sound.* | The object is probably of *irregular shape.* |
| (6) The weight of the box is felt when the object is at a particular side and also when it reaches the other side of the box by rolling or sliding. | There is a *feeling* of *heaviness* of the weight of the particular side of the box where the object remains. The object also strikes the other side of the box with a relatively heavy thrust. | The object is probably *heavy*. |

The experiments depicted above are by no means exhaustive but are only *typical*. Other appropriate experiments may be devised It should be stated about the above experiments that the students should be acquainted with the different *types* of sound, *viz*. rolling sound, sliding sound, rattling sound *etc*., and also the relative heaviness of the objects.

## PRACTICAL CHEMISTRY

Chemistry is an experimental science. The very essence of chemistry is its basic dependence upon experimental facts. There is no scope of guess-work of any sort in chemistry. Statements of any kind will have no value to chemists, unless and until they are seen to occur in reality. For this reason, chemists have greatest inclination towards exprimentation. They always prefer to work in the laboratory ; they observe the changes that occur and identify the products with certainty before making any general statement about them.

Students learning chemistry should similarly work in the laboratory to bear out the truths of the facts taught in their theoretical classes,by performing experiments themselves, since it is then and then only, the very concepts of the chemical phenomena are established in their mind, and in this way, the learning of chemistry becomes perfect. With this view in mind practical classes in chemistry are run side by side with the theoretical studies

The students of chemistry should seriously take notes of the lectures delivered by their teachers and learn from them the techniques of performing experiments They must bear in mind that only a skilled hand can reproduce the desired results through properly executed experiments, and so they should acquire that skill through repeated performance of the experiments.

To have such efficiency, they must acquire certain qualities which are essential for any one having a desire to learn chemistry. First of all, the students must love their laboratory and look at it with respect as a revered place, and they must protect their laboratory from any sort of damage. The students should be cautious of the fact that although the laboratory is an indispensible place for learning chemistry, it is a very dangerous place and any sort of accident may occur at any time, since there are so many inflammable substances as well as highly poisonous materials with which they are to work in the laboratory. The students must, therefore, remain always attentive while working in the laboratory, as any sort of carelessness may cause incurable harm. If, however, the students abide by certain rules and regulations,and are always attentive and remain cautious of what they are doing, they can easily come out with success without inviting any danger either to themselves or to the laboratory. The **do's** and **do not's**, which the students must follow while working in the laboratory, are given below :

## I. General Instructions.

(*i*) *Instructions for carrying out experiments in the laboratory:*

(a) Students should learn from their teacher what experiments they are to perform in their next practical class, and take notes of the lectures delivered by the teacher on those experiments.

(b) The theoretical back-ground and the procedures of those experiments should be fully understood by going through books and laboratory manuals, since shallow knowledge of the theoretical back-ground of the experiments often causes difficulty in performing experiments. Students should, therefore, prepare themselves at home, and if required, they should approach their teachers for having the subject clearly explained.

(c) Before commencing the actual experiment, the students should gather all the apparatus required, clean them properly and set up new equipments out of them as required for performing the particular experiment.

(d) Students should remember that it is a discredit to leave any experiment half-done They should be serious enough to complete the experiment, if required, through repeated attempts.

(e) While performing an experiment, the students **must** be attentive to observe the changes occuring. They are to take notes of these changes (of any kind) and draw possible inferences from these observations.

(f) Notes on the observations should be taken down, as soon as they are made, in a rough exercise book which should be submitted to the class-teacher just after the experimentation is over, on the same day, to get them approved and, if necessary, corrected.

(g) Students are to prepare their fair (laboratory) Note Book at home to keep records of the experiments peformed by them in the laboratory. These records are to be submitted in the examination and marks will be allotted according to the performance, as evidenced by their records. So, students should take particular care in writing down the fair note-books. These note-books must be *kept* carefully and no page from them should be torn off; they should be well-covered

(*ii*) *Instructions for preparing the fair (laboratory) note books.*

(a) The student should write his name, class, section, roll-number and the subject in bold letters on the cover of the laboratory note-book.

(b) The first two pages of the note-book should be left blank for writing *index*, which is done as shown below :

## INDEX

| *Serial No.* | *Date* | *Experiment* | *Page* | *Signature of the class-teacher* |
|---|---|---|---|---|
| 1. | 8.11 76 | Study of Bunsen burner | 1 | |
| 2. | | | | |
| 3. | | | | |

(c) Details of the experiments and observations are to be written in the ruled pages, while the blank left sides of the pages are to be kept for drawing sketches of the equipments used in performing the particular experiments. The description of the equipments should be written on the corresponding ruled pages on the right side.

(d) Details of the experimental work performed and the observations made therefrom are to be written on the ruled pages in the manner shown below :

1. The date on which the experiment is performed should be written on the left upper-most corner of the page.

2. The name of the experiment should be written in big bold letters as the main heading on the top of the page.

3. Experimental details are to be written under the following headings in different paragraphs ; (1) General principle (or Theory) of the experiment, (2) Apparatus required, (3) Chemicals or materials required, (4) Experimental procedure, (5) Results and lastly (6) Precautions.

The results of experiments should always be recorded in a tabular form as shown below :

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| | | |

N. B. (1) The fair laboratory note-book should be written and submitted to the class-teacher in the next practical class and got it duly corrected and signed.

(4) Since without the fair laboratory note-book, the students may not be permitted to sit for the final examination, they should take particular care of the note book, so that it is not lost or damaged in any way.

**II. Instructions for general attention and behaviour in the laboratory.**

(i) In the laboratories, there are substances, some of which are highly inflammable, some are highly poisonous, while some others are explosive. So, the students must always remain attentive and cautious of what they are doing, and with what substances.

(ii) Idle gossiping must not be done while working in the laboratory. To be absent-minded is a serious offence while working in the laboratory, since it may lead to dangerous accidents.

(iii) The **garments** which the student wear at the time of working in the laboratory, should always be **tight fitting. It is** inconvenient as well as risky to wear loose garments during practical work, for they may catch fire or may be spoilt by acids and other chemicals. The students are advised to **put on apron**, or use a towel tightly around their waists.

(iv) The students should have, along with their books and notes, a pen-knife, a match box, a ruler, a **piece of cloth or** towel and a piece of soap. After the laboratory work, **hands must be washed with soap.**

(v) Students **should not touch** any chemical with the hand ; the solid chemicals should be taken with the help of a spatula and liquids should be transferred with test tubes, beakers, basins or any other vessel.

(vi) Students **must not taste any chemical**. It is to be remembered that most of the chemicals are **poisonous.**

(vii) While setting up an apparatus for performing experiment, the students should be particularly careful to see that the fittings are not loose.

(viii) Hot glass apparatus, or burners which have struck back should not be touched with hand ; they may cause serious burns.

**III. Instruction for the use of equipments, reagents, gas, water etc. in the laboratory :**

(i) Students should be cautious and economical in using gas, water etc. in the laboratory. Gas taps and water taps must not be kept turned on ; they should be opened only when they are required, and after the use, they must be turned off. Burners should be extinguished when they are not in use, and even while working, the size of the flame should be kept as small as possible (except when strong heating is essentially required) to avoid unnecessary wastage of the gas.

(ii) Students should take particular care of the reagent bottles. The bottles must not be left on the table, but should be kept in their proper places on the racks. They must always be stoppered properly.

(iii) If any reagent bottle loses its label, it should be immediately labelled, since it is unwise to use reagent from a bottle having no label. The student should, therefore, be careful also in handling reagent bottles so that their labels are not torn off.

**IV. Precautionary measures to be taken during performing experiments.**

(i) While heating acids, ammonia or other strong chemicals in a test tube, the students should hold the test tube *away from their eyes (and below the eye-level)* in such a manner that in case the liquid inside spurts, it may not strike his eyes or any part of his face. (ii) While warming anything in a test tube, it should be held by means of a test-tube holder or by a fold of paper; filter papers should never be used for this purpose. (iii) While heating a solution or any other liquid, especially those containing strong acids or alkalis, students should be particularly watchful, and control the burner-flame so that heating is started very slowly. Stronger heating may follow, if required. (iv) Remember that the wash-basins are meant for drainage of waste water, liquids, chemicals etc. So, anything else, especially the solid materials like waste papers (including filter papers), broken glass rods or glass apparatus, match sticks *etc.* must not be thrown into the basin, as the outlet tube of the basin may be choked and the basin will not work for drainage of waste liquids.

(v) Basins are made of such materials as are attacked by strong acids as well as strong alkalis. So, when hot concentrated acids or alkalis are thrown into the basin, sufficient water should be poured in it by turning on the water taps.

**Accidents and Remedies.**

While working in the laboratories, students sometimes meet with minor accidents which are often due to their carelessness. If, however, the students remain particularly watchful and attentive, many minor accidents can be avoided.

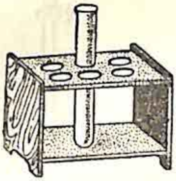
The accidents that generally occur in the laboratory are of the nature of : (*a*) *burns* (*b*) *cuts* and (*c*) *gas-poisoning.*

(a) **Burns.**—For burns, medicines like Burnol, or in its absence substances like olive oil, cocoanut oil, vaseline with picric acid or boric acid, or vaseline alone may be applied on the affected part(s). In cases of acid burns, however, the affected parts should be washed with water and then with a very dilute solution of sodium carbonate and finally, vaseline should be applied.

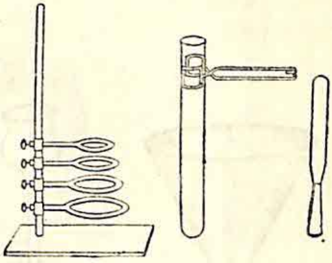
(*b*) **Cuts.**—In case of cuts, the wound should be first cleansed with water and then with Dettol or tincture of iodine and finally, if necessary, it may be sealed with tincture benzoin. If the cut is due to broken glass, any minute particles of glass that may remain in the wound should be removed first.

(*c*) **Gas-poisoning.**—Many gases, evolved during experiments, are suffocating and/or poisonous. If a student feels discomfort after inhaling such gases as hydrogen chloride, sulphuretted hydrogen, chlorine, sulphur dioxide or certain acid vapours, relief may be obtained by inhaling ammonia gas from a bottle containing dil. $NH_4OH$ soln. for some time, or merely by breathing fresh air in an open space outside the laboratory. For more serious cases of poisoning, the teacher in charge of the laboratory should call for immediate medical attention by properly qualified physician. It is essential to provide a **First Aid Box** containing all the necessary medicines and antiseptics and other commodities for taking immediate action against minor accidents in the laboratory.

# SOME OF THE APPARATUS COMMONLY USED IN THE LABORATORY

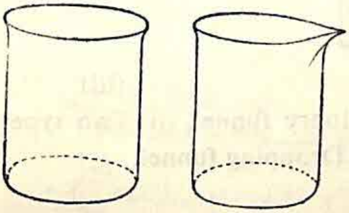


Test tube in wooden test tube stand.



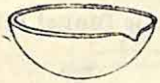
(i) (ii) (iii)

(i) Rings clamped in stand (ii) Test tube with test tube holder (iii) Spatula.

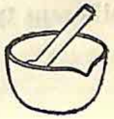


(i) (ii)

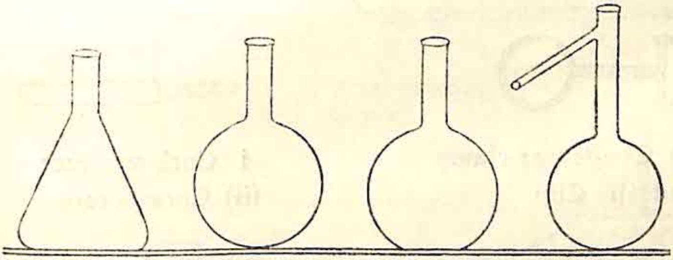
Beakers : (i) without lip
(ii) with lip.



Porcelain basin

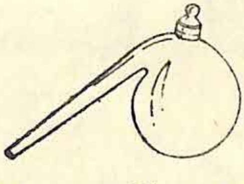


Mortar and Pestle

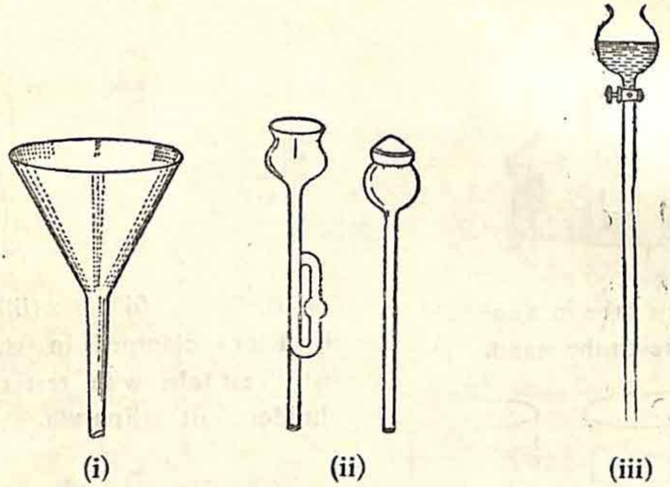


(i) (ii) (iii) (iv)

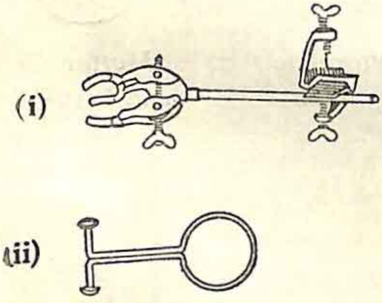
Different types of flasks : (i) Conical flask, (ii) Round-bottomed flask, (iii) Flat-bottomed flask. (iv) Distilling flask with side-tube.



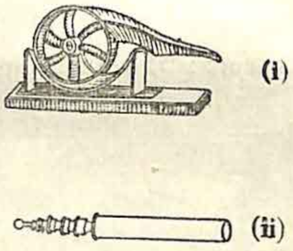
Retort with stopper



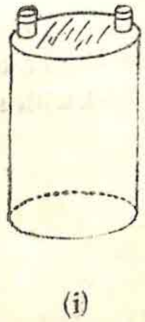
Different types of funnels : (i) Ordinary funnel, (ii) Two types of thistle funnel, (iii) Dropping funnel.



(i) Condenser clamp
and (ii) Clip.

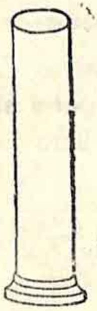


(i) Cork-squeezer
(ii) Cork-borers.



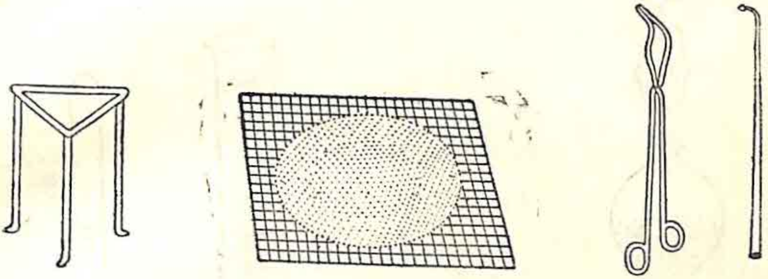
(i)

(i) Woulr's bottle



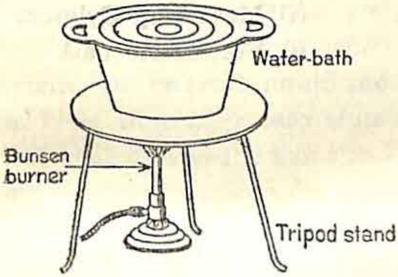
(ii)

(ii) Gas-jar

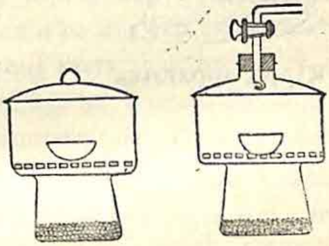


(i) (ii) (iii) (iv)

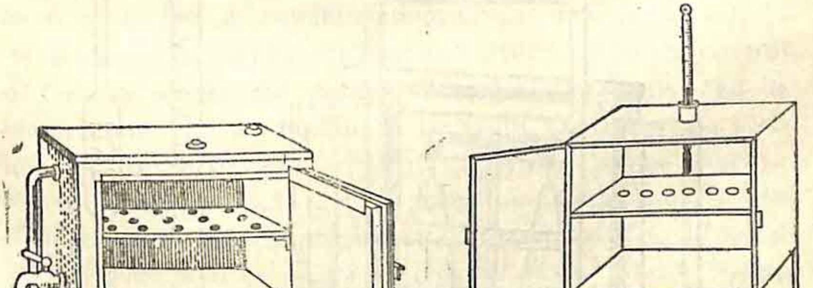
(i) Tripod stand, (ii) Wire-gauze, (iii) Tongs, (iv) Blow-pipe.



Water-bath

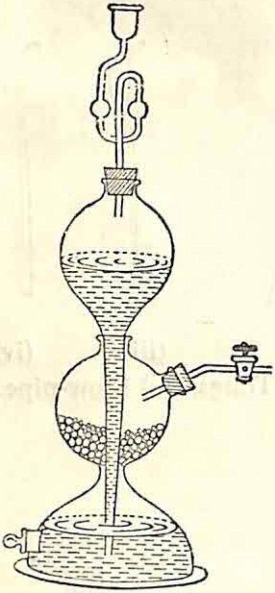


Desiccator (ordinary & vacuum)

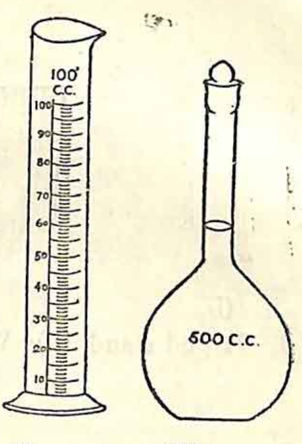


(i) (ii)

Two diffierent types of ovens : (i) Steam oven, (ii) Air oven.

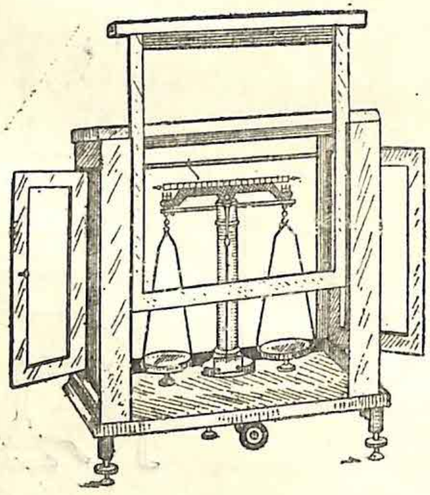


Kipp's apparatus

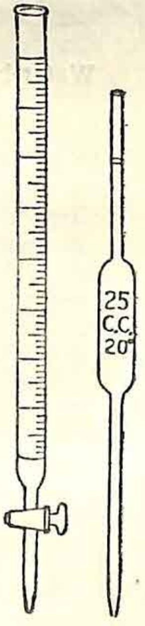


(i) (ii)

(i) Measuring Cylinder
(ii) Volumetric flask



Chemical balance.



Burette & Pipette

## 1

# STUDY OF BUNSEN BURNER AND ITS FLAME

**Burners :** To perform some chemical tests or to carry out some experiments involving chemical reactions, application of heat is necessary. Although it is easy to produce heat by burning wood or coal or any other combustible matter in ordinary ovens, the latter are not suitable for use in laboratories, since experimentations essentially require sophistication and control of flame or tempepature, which cannot be done with ordinary ovens. Of the solid, liquid and gaseous fuels, it is the last class of fuels that offer maximum advantage as regards flexibility and control over the flame and its temperature. Gaseous fuels are also advantageous for their easy availability, maintenance and cleanliness. For these reasons, gaseous fuels are very suitable for laboratories. But, for burning gaseous fuels, some special mechanical devices are required which would allow the gas to burn without causing disturbance or danger. Such devices are called *burners.* A burner should be so designed as to burn the maximum amount of gas flowing into it, to produce maximum possible heat and also to allow the control of fuel to obtain the desired nature of the flame and its temperature. Such a burner, as is usually and ordinarily used in the laboratories, was first devised by the German scientist, Robert Bunsen, in 1855 and as such, these burners are known after the name of their discoverer as **Bunsen burners.** *Thus, a Bunsen burner is a simple mechanical device (discovered by Robert Bunsen) used in laboratories for producing heat and flame by burning gaseous fuel (commonly coal gas).*

[Petrol gas or '*Gobar gas*' is also used in some places.]

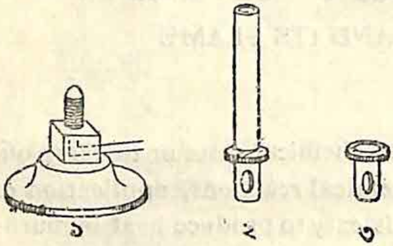
**Description of the Bunsen burner : Its structure and working principle.**

*Structure* **:** A Bunsen burner is generally made of brass and iron and has three parts in combination **:**

*(a)* a **base**, *(b)* a burner tube or barrel and *(c)* a ring with a hole.

*(a)* The **base** (made of cast iron) is fitted with a narrow nozzle (jet) at the centre and an inlet tube at one side (both made of brass), which are in communication with each other through the body of the base.

The nozzle is provided with screw-thread on its outer surface to which the burner tube is fitted. The inlet tube allows coal gas to flow in and its speed is increased by passing through the narrow nozzle which throws the gas in a fine jet upwards through the burner tube.



(i) base, (ii) barrel, (iii) ring.
Fig. 1-1. Three main parts of a Bunsen burner.

*(b)* The **burner tube** (also called **barrel**) is a narrow cylindrical pipe (made of brass) of varying length depending upon the overall size of the burner. It has, at its lower end, air-hole either on one side or on both diametrically opposite sides, linearly with the tip of the inlet jet

*(c)* The **ring**, also called the **air-regulator** or **collar**, is an annular ring (made of brass) fitted over the burner tube at the junction of its lower end and the base. The ring has holes corresponding to the number of air-holes in the barrel. The ring is so placed round the barrel that its holes exactly align themselves with those of the barrel. The ring can be rotated round the burner tube, and the air-holes can be made *fully open*, *partially open* or *fully closed* by rotating the air-regulator and thereby regulating the access of air into the burner.

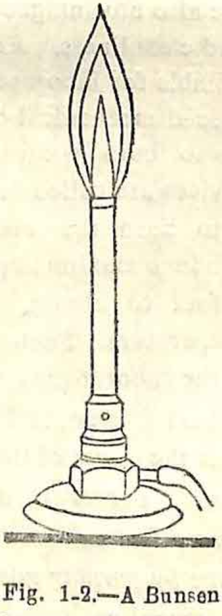


Fig. 1-2.—A Bunsen burner with all parts duly fitted together.

*Working principle* : The burning of coal-gas and the heat produced therefrom can be regulated by controlling the volume of air that mixes with it. In a Bunsen burner, the amount of air is controlled by regulating the opening of the holes on rotating the air regulator. The coal-gas enters through the side-tube (inlet tube) and is pushed up in a jet by the nozzle. The rapidly moving gas draws in air through the air-holes, the mixture of gas and air passes up through the barrel and it burns at the mouth when ignited, producing a flame.

**Flame.**—A flame is produced only during the combustion of a gas or a vapour. It may be defined *as a zone or bounded area in which chemical reaction (combustion) is occuring, attended by the evolution of heat and light.*

The flame produced in the Bunsen burner is formed by the combustion of coal gas in air (oxygen).

**Types of Bunsen flame: Their structures and characteristics.**

By adjusting the air-regulator, two types of flame can be produced at the top of the burner tube by burning coal-gas, *viz.* (*a*) *Luminous flame ānd* (*b*) *Non-luminous flame.*

(*a*) **Luminous flame :** When the air-holes of the burner are kept completely closed, the flame obtained from a Bunsen burner is luminous, having a yellow colour similar to that of a candle flame. This is also known as the *reducing flame*. The luminosity of the flame is mainly due to the presence of heated but unburnt solid carbon particles formed through the incomplete combustion of the gas in limited supply of air. The luminosity of the gas is also affected by the pressure of the incoming gas and by its temperature.

**Structure of the Luminous flame**—The luminous flame of a Bunsen burner is made up of four zones : (1) The small cup-like **blue zone** (*a*) at the base of the flame The blue colour of the flame here arises from the burning of carbon monoxide formed through incomplete combustion of coal-gas.

(2) The **dark central zone** (*b*) in the lower middle part of the flame. This is a zone which accommodates unburnt gas. Here no combustion occours and hence, this zone remains cold.

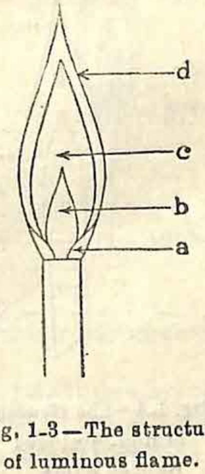


Fig. 1-3—The structure of luminous flame.

(3) **The bright luminous zone** (*c*) surrounding the dark zone. Here the gas burns with the little air supplied at the base of the burner and hence, combustion takes place incompletely, for which a blue colour develops.

(4) **The non-luminous outer zone** (*d*) surrounding the entire flame. Here the gas burns completely with air supplied from outside.

(*b*) **Non-Luminous flame.**—When the air-holes of the Bunsen burner are kept open, a non-luminous and much hotter flame is produced. It is also known as *oxidising flame* Such a flame is non-luminous mainly due to the complete combustion of the fuel gas, leaving no carbon particle unburnt, and this imparts non-luminous character to the flame. Complete combustion of the gas is effected because of the fact that, with the air-holes completely open, sufficient air is sucked into the burner, which mixes up with the gas and supplies sufficient oxygen required for the complete combustion of the gas.

**Structure of the non-lumnious Flame.**—The non-liminous Bunsen flame consists of two zones :

(i) the inner bluish-green zone (a) consisting mainly of unburnt gases.

(ii) an outer mantle (b) where complete combustion of gases occurs.

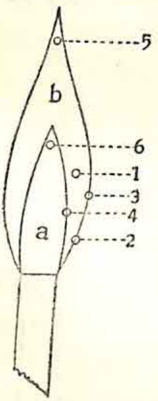


Fig. 1-4—The structure of non-luminous Bunsen flame.

The principal parts of this non-luminous Bunsen flame are clearly shown in the figure 1-4,

The **lowest temperature** is at the base of the flame (2) , this is employed for testing the volatility of substances in order to observe whether they impart any colour to the flame (*Flame Test.*).

The **hottest part** of the flame is the *fusion zone* (1) which lies at about one, third of the height of the flame and is approximately equidistant from the outside and inside of the mantle. It is employed for testing the fusibility of substances and also in conjunction with(2), in testing the relative volatilities of substances.

The **lower oxidising zone** (3) is situated on the outer border of (1) and may be used for the oxidation of substances dissolved in *beads of borax*, sodium carbonate (or microcosmic salt).

The **upper oxidising zone** (5) consists of non-luminous tip of the flame ; here a large excess of oxygen is present and the flame is not so hot as at (3). It may be used for all oxidation processes in which very high temperature is not required.

The **upper reducing zone** (6) is at the tip of the inner blue cone, and it is rich in incandescent carbon ; it is especially useful for reducing metallic oxides to the metals.

The **lower reducing zone** (4) is situated in the inner edge of the pale blue-zone next to the blue cone and it is here that the reducing gases mix with the oxygen of the air ; it is a less powerful reducing zone than (6 and may be employed for the reduction of fused borax and similar beads.

**Experiments to show the structure of Bunsen flame.**

**Experiment** 8) : *To show that the inner-most zone at either type of flame—luminous or non-luminous—is a cone full of unburnt gas.*

A Bunsen burner is taken. The side-tube at its base is connected with the help of India-rubber tubing to a gas tap to flow gas into the burner and the gas is ignited at the mouth (upper end) of the burner tube, when a flame will be obtained.

At first, the air-holes are kept completely open when the flame will be non-lumnious and the dark inner-zone will be detectably visible (an adjustment of the air-regulator may be required). Now, a glass tube, with both the ends open, is introduced inside the flame so that its one end reaches the dark inner-most zone of the flame, while at the other end an ignited match-stick is held. A flame will be produced within a short time. It proves that the unburnt gas, accumulated in the

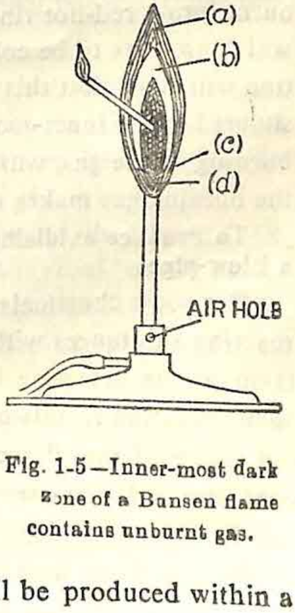


Fig. 1-5—Inner-most dark zone of a Bunsen flame contains unburnt gas.

inner dark zone of the Bunsen flame, comes out through the glass tube and produces at flame at its other end on ignition.

The experiment is repeated with air-holes fully closed (*i e.*, with luminous flame) and similar observation may be made.

**Experiment (2) :** *To show the existence of a zone of unburnt gas and zones of varying heat, of a Bunsen flame.*

(1) A piece of a thin card-board (or a paper) is placed horizontally in such a height of the Bunsen flame as to cross past both the zones of the flame for a short while and removed just before burning would occur. It will be observed that the affected part of the board (paper) forms a ring (Fig. 1-6). It proves that the inner zone causes no burning while the hot parts of the flame turn the board (or paper) brown.

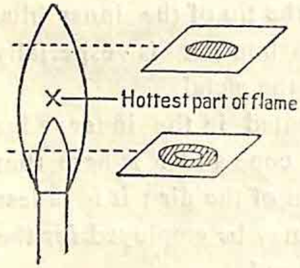


Fig. 1-6—Experiment to show the temperature of the different parts of a Bunsen flame.

(2) Alternatively, a copper wire-gauge is held with the help of tongs, in the flame for some time. It will be observed that the part of the wire-guage affected by hot flame has been burnt into a red-hot ring surrounding a circular dark portion which appears to be cold and not affected at all. An inspection will show that this cold, dark part of the copper gauze is situated in the inner-most zone of the flame, where occurs no burning of the gas, while outside this zone, the hot flame of the burning gas makes the copper gauze red-hot.

**To Produce oxidising and reducing flames with the help of a Blow-pipe.**

For some chemical reactions, it is often required to heat the reacting substances with the Bunsen flame directly impinging on them, *e g.* in detecting basic radicals on charcoal blocks. In such cases, the results of heating depend to a greater extent on the nature of the flame. So, for such tests to be performed correctly, it is necessary to produce the correct type of flame (oxidising or reducing) required. This can be done by blowing the Bunsen flame with the help of a blow-pipe. Two different techniques of blowing produce two different types of flames. A luminous flame (air-holes completely closed), about 2 inches long, is employed for these purposes

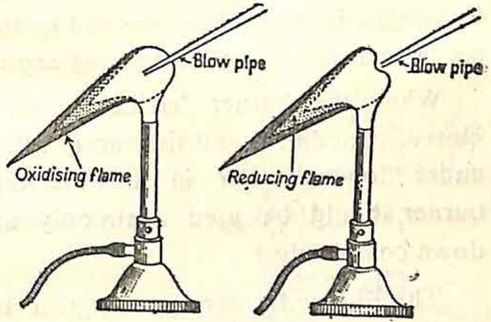


Fig. 1-7.—Production of oxidising and reducing flames using a blow-pipe.

*To produce oxidising flame using a blow-pipe*: An oxidising flame is obtained by holding the nozzle of the blow-pipe about **one-third within the** luminous Bunsen flame and blowing hard (vigorously) from the cheeks (and not from the lungs) in a direction parallel to the burner top ; a jet of non-luminous flame is produced. The extreme tip of the flame-jet is allowed to play upon the substance under test, since it is this part of the jet which is oxidising.

*To produce reducing flame using a blow-pipe* : A reducing flame is produced by keeping the nozzle of the blow-pipe **just outside** the flame and blowing gently so as to cause the luminous flame to deflect from its vertical position and play upon the substance on the charcoal block. Under this condition, the flame is mostly reducing.

**"Striking back" of a Bunsen flame.**—At times, especially when the pressure of the gas is low, and the su ply of air is too much, the Bunsen flame is found to be drawn back within the burner tube and to burn at the mouth of the inlet-nozzle. This occurrence of burning of the gas at the mouth of the nozzle within the burner tube is termed the '*Striking back*' of the flame.

'*Stricking back*' occurs due to the irregular supply of gas relative to the supply of air. There is a limit to the amount of air which should be supplied by the holes in the Bunsen burner at the base. If the amount of air introduced at the base is sufficient to cause almost complete combustion, and the rate of burning the mixture exceeds the speed at which the gas is moving up the tube, the flame 'strikes back.'

This 'striking back' of the flame is **dangerous**, because the tube and the base of the burner will become hot enough to produce serious burns when touched, and occasionally the burner melts the rubber tube and ignites the gas near the gas-tap, which may cause devastating explosion.

When the burner 'strikes back', the gas tap should be closed immediately and the burner allowed to cool (by holding under flowing water in a water-tap, if necessary). The burner should be used again only after it has been cooled down completely.

The Bunsen burners are of great use, rather indispensible, in the laboratories. Temperatures as high as 1500° C (generally 700°– 800 C is maintained) can be attained. With some modifications, these burners are used for heating incandescent mantles in gas-lighting. The only draw-back is the tendency to 'strike back' when the supply of gas is reduced below a certain limit. The 'striking back' may be avoided by covering the top of the burner with a metal gauge which controls the ratio of gas and air in the burning mixture and hence, controls the combustion, and it also does not allow the flame to pass down into the burner tube. This is done in some modern types of burners and stoves.

**Other types of burners.**—Some types of burners, other than the Bunsen burner, which are in common use in laboratories are : (i) **Meker burner** (ii) **Teclu burner** (iii) **Ring burner** (iv) **Fish-tail burner etc.**

Each of these burners are endowed with some special advantages and are used for certain particular purpose For example, **Meker burner** [Fig. 1-8(a) is so designed that it can make use of higher proportion of air with the gas, which cannot be done in a Bunsen burner due to the danger of 'striking back'. For complete combustion of coal-gas, a proportion of 6 volumes of air to one volume of the gas is required, while the proportion of air and gas producing normal Bunsen flame is about 2·5 volumes to 1 volume. So, the Bunsen burner cannot make use of the total heating capacity of the fuel gas, and also it is not without the danger of 'striking back'. These two difficulties are overcome in a Meker burner which are provided with larger air-holes which supply air required for compelete combustion of the fuel gas and it is provided with a wider barrel with a nickel or copper grid (or wire-gauge)

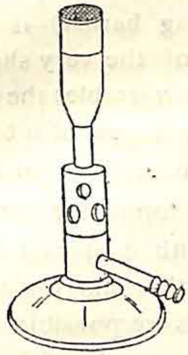
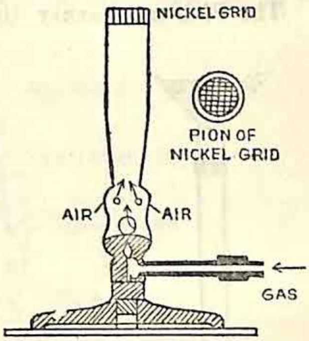


Fig. 1-8(a)—Meker burner.



Fig, 1-8(b).—The structure of Meker burner.

placed at top (Fig. 1-8(b)], which prevents the flame from striking back. Thus, in a Meker burner, a temperature of 1100°—1200°C can be ordinarily attained without danger.

**The Ring burner** (Fig. 1-9) may be considered as made up of a series of small Bunsen burners placed in a circle with a cast iron setting. It is widely used in laboratories as well as in cooking (domestic), where large vessels are to be heated more or less rapidly and uniformly.

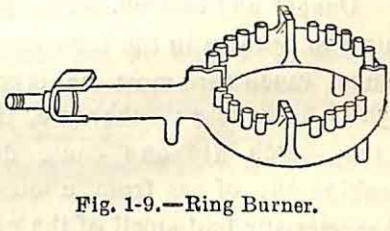


Fig. 1-9.—Ring Burner.

**A Teclu burner** is a modified type of an ordinary Bunsen burner. Its barrel is of the shape of a conical drum at the base. A brass circular disc can be raised up or lowered down by a screw-arrangement (along gas-inlet nozzle at the base of the burner) to allow opening of different amounts for the introduction of varying quantities of air in the

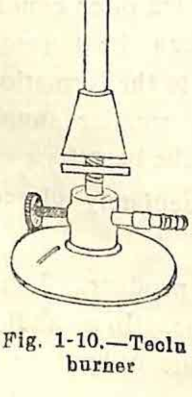


Fig. 1-10.—Teclu burner

burner. Temperatures higher than those attained in a Bunsen burner can be obtained by this burner.

**The Fish-tail burner** (also called **Bats-wing burner**) is so-named because of the very shape of its flame which resembles the tail of a fish (or the wings of a bat). The burner has no air hole or air-regulator and the top of the burner tube is fitted with a special cap provided with a thin narrow slit-opening which is responsible for producing the flame of a fish-tail shape.

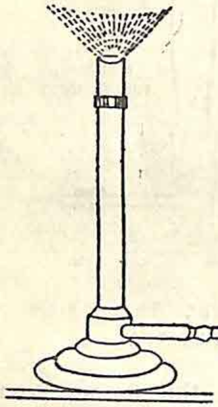


Fig. 1-11—Fish-tail burner

This burner produces a luminous flame which is thin and widened and as such, it is best suitable for bending glass tubes, because it can heat uniformly a large area of the tube.

**Danger and caution.**—The gas (coal-gas) that is usually burnt in burners in the laboratories are highly inflammable and hence, much care must be taken in turning off the gas taps tightly after use; otherwise, if gas leaks out from any tap, it may catch fire and cause devastation in the laboratory. Leaking out of gas from a loose tap may be detected by the characteristic bad smell of the gas, and if such thing happens, the tap should be detected immediately and properly tightened. 'Striking back' of burner is another danger which often causes painful burns. If any burner strikes back, it can be detected by the foul smell near about that burner (due to the formation of $C_2H_2$ during 'striking back') and also by a peculiar sound produced due to the burning of the gas inside the barrel.

If it so happens, the gas tap must be immediately closed and the burner allowed to cool.

**Candle Fame.**—A wax-candle, on burning, produces flame which is more or less similar to a Bunsen flame. In a candle, the flame is produced by the burning of vapours of hydrocarbons which, in the solid state, are the constituents of wax. The different regions of a candle flame are shown in the figure. A candle flame is not generally used in a chemical laboratory due to the facts that the flame cannot be regulated as in a burner and the heat obtained from such a flame is generally less than that obtained in a burner. Further, much of the material of the candle (wax) is wasted in the form of liquid (molten wax) during the burning of a candle.

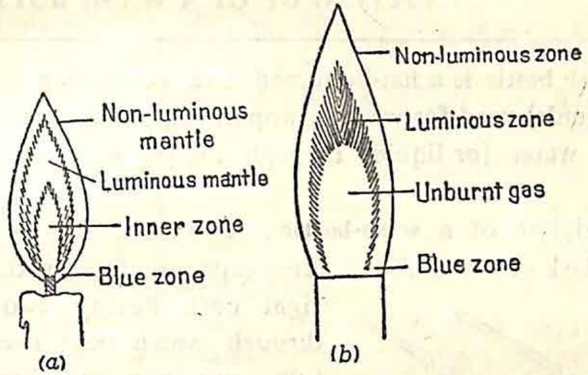


Fig. 1-12.—Candle flame *vs.* Bunsen flame.

## ORAL QUESTIONS

1. What is a burner ? What kind of burner is usually used in laboratories ?
2. Why Bunsen burners are provided with air-holes ?
3. Are air-holes essential for burning gases in burners ?
4. When the air-holes are closed, why does not the burner go off ?
5. What is 'striking back' of a Bunsen burner? If a Bunsen burner 'strikes back', what would you do ?
6. What do you mean by a 'flame' ? What different types of flames can be produced in a Bunsen burner ?
7. What are the essential parts of an oxidising flame ?
8. What are the essential parts of a reducing flame ?
9. Where lies the hottest part within a Bunsen flame ?
10. Where lies the reducing zone within an oxidising flame ?
11. Why sometimes does the Bunsen flame develop a blue colour ?
12. What is there within the inner-most darker part of a Bunsen flame ?
13. What is a Meker burner ? What is the Fish-tail burner ? Why is it so called ?
14. How would you heat a body with an oxidising flame directly falling upon it ?

2

## FITTING AND HANDLING OF APPARATUS.

### FITTING UP OF A WASH BOTTLE

**A wash bottle** is a flat-bottomed flask containing water (or other liquids) used for washing apparatus, precipitates *etc.* by blowing water (or liquid) through the jet with which it is fitted.

**Description of a wash-bottle :** A wash bottle is a flat-bottom flask of 500 ml. (or 1 litre) capacity, fitted with an air-tight cork having two holes, through which pass two glass-tubes, one long and bent at an acute angle near one of its ends and the other short and bent at an obtuse angle in the middle. The two angles of the two tubes are so made as to form about 180° together. The cork, along with the tubes inserted through it, is carefully fitted to the flask to make air-tight joints. The longer arm of the acute-angled tube reaches almost to the bottom of the flask and the other arm remains outside the flask and is connected with a jet (made of glass tube) by means of a piece of rubber-tubing. On the other hand, one arm of the obtuse-angled tube extends a little beyond the cork inside the flask, the other arm remaining free to serve as mouth-piece for blowing. About three-fourths of the flask is filled with distilled water (Fig. 2-1).

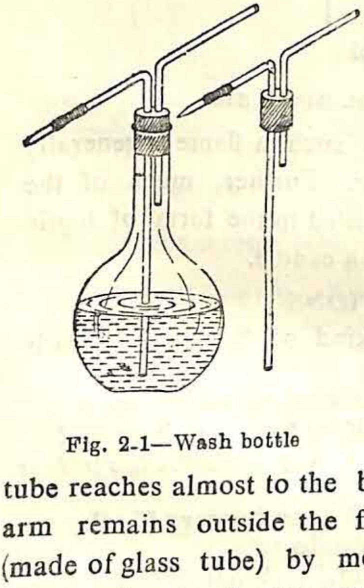


Fig. 2-1—Wash bottle

Uses : A wash bottle is indispensible in a chemical loboratory for washing purposes and for transferring precipitates adhering to the vessel to a filter. It is also used to add controlled amount of water, as in the case of making up of volumes of standard solutions. When air is blown through the mouth-piece (obtuse-angled tube), water is forced out through the jet in a very narrow stream which is played on the apparatus or the precipitate to be decanted and washed, or the outcoming water is added at a controlled rate to the standard solution in a volumetric flask.

**To Fit Up a Wash Bottle :** In order to fit up a wash-bottle, the following operations are to be performed :

(i) *Cutting two pieces of glass tube and rounding the sharp edges (fire-polishing).*
(ii) *Bending glass tubes.*
(iii) *Drawing a jet.*
(iv) *Boring a cork.*
(v) *Fitting up the wash bottle.*

Expt. (i)—CUTTING A PIECE OF GLASS TUBE AND ROUNDING THE SHARP EDGES *(fire-polishing).*

**Meterials needed** —A triangular file, a Bunsen burner, an asbestos board and a glass tube of narrow bore (about 4-5mm. diameter).

**Procedure.**—The glass tube is placed on the table and is held tightly against the table with the left hand, while with the right hand is held the triangular file which is placed upon the glass tube on the point at which the tube is to be cut. Now, by a sharp drawing (in one direction only) of the file over the glass tube at that point, a scratch is made upon the glass, If the impression of the scratch is not well, the file may be placed again on the point and the operation repeated. For breaking the glass tube at the point of scratch, it is held with both hands (preferably wrapped with a towel), placing the thumbs right opposite the scratch (as shown in the figure 2-2) and a gentle pressure is applied, when the tube breaks along the scratch into two portions, having very sharp and uniform edges. The operation is repeated to have three pieces of glass tubes, two of larger size, ∼25 cm. and ∼15 cm. in length, and a shorter one of length ∼5 cm.

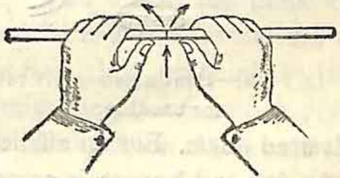


Fig. 2-2—Cutting the glass tube.

*Rounding the sharp edges :* The sharp edges of the freshly-cut glass are dangerous to handle, since they may cause cuts and bruises in hands due to unmindful handling. So these sharp edges are rounded by holding them in burner flames.

To do this, a Bunsen burner is lighted and the sharp edges of the newly cut tubes are held over the flame and rotated slowly until the sharp edges just melt and get rounded up (Fire-polishing). The tubes with hot ends are kept on asbestos board for cooling slowly.

### Expt. (ii)—BENDING OF TUBE.

**Apparatus.**—Glass tubes, fish-tail burner and an asbestos board.

**Procedure.**—To bend a glass tube (or a glass rod), it is held over the flame and the part to be bent is placed inside the flame and rotated by finger, so as to heat the part of the glass tube uniformly on all sides [Fig. 2-3(a)] After a short while, the glass will be soft at the hot part and tends to bend by itself over the flam. It is then taken out of the flame and placed on asbestos board and mild pressure is applied on either side to get it bent of a desired angle. For an efficient performance of the process, use of a fish-tail burner is recommended, since it would heat a greater part of the glass tube uniformly at a time [Fig 2-3 a)]. The angle at which the tube is to be bent may be kept drawn on the asbestos board, so that the desired bending is done accurately within a short time before the hot tube gets cooled and stiff to oppose bending [Fig. 2-3(b)]. It is advisable that, during application of pressure on either side of the tube to get the hot part bent, care must be taken to see that the pressure is

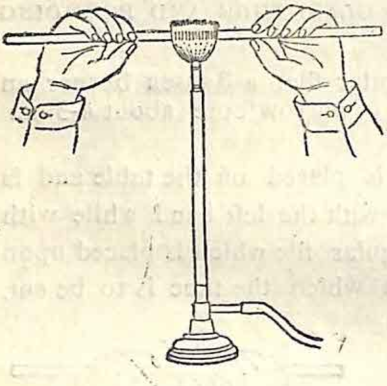


Fig. 2-3(a)—Heating the glass tube for bending.

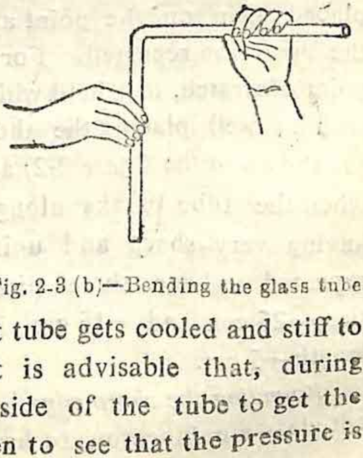


Fig. 2-3 (b)—Bending the glass tube.

very small and applied gently and slowly to have the bend uniform ['A' in Fig. 2-3(c)]; otherwise the bending will not be uniform, constrictions would be produced ('C' in the fig.) in the curved part, and/or there would occur flattening of the surface of the tube ('B' in the fig.).

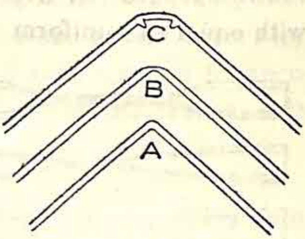


Fig. 2-3(c)—Correct (A) and incorrect (B, C) bending.

For fitting up a wash bottle, the two long glass tubes are to be bent at the desired angles. The longer tube (this should be about 12 cm. longer than the height of the flask to be used) is to be bent at an acute angle (45°) at a point about 5 cm. from one end, and the shorter one is to be bent at the middle at an angle of 135°

It is convenient to have the angles 45° and 135° drawn at a little distance on an asbestos board. The fish-tail burner is lighted and the longer tube is held with both hands in plane with the flame (not across the flame) and the part (5 cm. from one end) to be bent is placed inside the flame and kept rotating till the heated portion becomes just soft and tend to bend over the flame. The hot tube is then taken out of the flame and placed on the asbestos board where the acute angle was drawn. Now, mild pressure is applied on both sides to bend the tube upto the desired angle (45°), keeping the entire length of the tube on the asbestos board. It is then left on the board and allowed to cool slowly (*annealing*). In a similar way, the other tube (15 cm. long) is bent at the middle upto the desired angle (135°) and allowed to cool.

Expt. (ii)—DRAWING A JET.

**Apparatus.**—Glass tubes and a Bunsen burner.

A glass tube, one end of which is drawn to a narrow point (but not sealed off) is called a jet To draw jets, the glass tube is to be heated in the middle strongly and uniformly on a Bunsen flame (but a roaring flame should be avoided), as des-

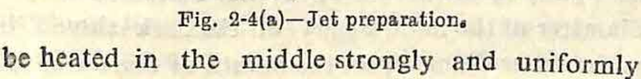


Fig. 2-4(a)—Jet preparation.

cribed above, when the hot part will rapidly soften. The tube is then taken out of the flame and the two ends of the tube are drawn outwards, at first slowly, and then quickly at a time with equal and uniform force, when the heated soft portion gets elongated and converted into a narrow capillary at the middle. The tubes is then placed on an asbestos board and allowed to cool. After cooling, the elongated portion is broken at the middle and thus two jets are obtained. During drawing the jet, care must be taken so that the two ends of the tube are held straight and tightly ; otherwise, the drawing will not be uniform and the jets will have bends and kinks rather than being uniformly straight. Further, equal outward pressure must be applied on both sides, otherwise, the elongation will not be uniform, and one of the jets will be very thin and short while the other will be long and of wider bore.

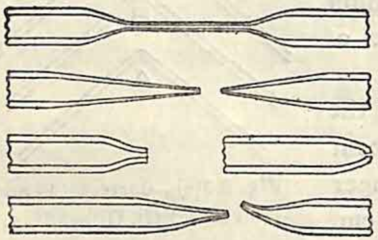


Fig. 2.4(b) -Different types of jets.

Different types of jets are required for different purposes ; these are prepared in the same way as stated above, but with careful manipulation of pressure and drawing and of the time of heating. For fitting in a wash bottle a jet of about 1 mm. bore and 2 cm. narrowed end is suitable,

For wash bottle, a jet is required to be connected to the shorter limb of the longer bent tube. [To prepare the jet, a tube, 5 cm. long, is heated in the middle on a flame of a Bunsen burner and when the heated part has sufficiently softened, it is drawn into a jet in the way described above ]

Expt. (iv)—BORING A CORK.

**Apparatus.**—A cork, a cork-squeezer and a cork-borer.

**Procedure :** *Choice of cork.*—The cork to be bored should be carefully chosen. A cork should be so selected that it fits well and tightly to the mouth of the flat-bottomed flask. The outer diameter of the middle part of the cork should be the same as the inner diameter of the mouth of the flask, so that half of the cork goes in and half extends out. For tight-fitting of the cork to an opening, a cork of slightly bigger size is to be selected first, which is then squeezed by the cork-squeezer (carefully, so that the cork does not crack) after softening it by soaking in water. After one or two squeezing, the cork will just fit in the opening and such a fitting is expected to be air-tight. It is desirable to use a cork (velvet) with less pores.

*Boring of the cork* —To bore a cork, cork-borers are used. Cork-borers may be of differsnt size and shape. But, the borer to be chosen for boring should have a slightly smaller diameter than the outer diameter of the tube to be fitted to that bore. For boring, the selected cork is first softened with water, squeezed by the cork-squeezer to the desired shape and size and then placed on a table with its narrower flat end upwards. The position where the bore is to be made is marked and the borer is placed on this mark (Fig. 2-5).

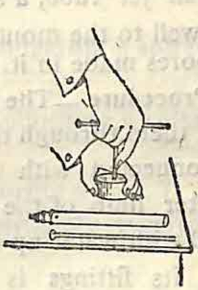


Fig. 2-5.—Boring of a cork.

Boring is then done by pressing the borer and driving it downards like a screw. After a little endeavour, the borer will pass through the cork to the other side ; it is then pulled out and thus the desired bore is obtained. During boring, care should be taken to see that the borer always remains perpendicular to the flat surface of the cork ; otherwise the bore will not be vertical and the fittings made afterwards will not be uniform.

For fitting up a wash bottle, the cork to be placed at the mouth of the bottle is properly chosen and two positions are marked side by side where the borings are to be made. The suitable chosen borer (of diameter slightly less than the outer diameter of the tubes to be pushed in through the bores). is placed on the marks and borings are done one after another in the same way as described above. In this case, it should be noted that, as two bores are made side by side, sufficient care must be taken during boring so that the bores are uniform and vertical (parallel to each other). If the cork cracks or the bores are not parallel and not in the mid-plane, it should be rejected.

### Expt. (v)—FITTING UP THE WASH BOTTLE.

**Materials.**—A flat-bottomed flask of 500 ml. (or 1 litre) capacity, two glass tubes, one bent at an acute angle (45°) with one longer limb and the other bent at an obtuse angle (135°), a small jet tube, a small piece of rubber tube and a cork that fits well to the mouth of the bottle and has two parallel vertical bores made in it.

**Procedure.**—The bent tubes are fitted to the cork by inserting them through the bores, one in each. The small jet tube is connected with the help of a small rubber tubing to the shorter limb of the tube bent at an acute angle. The flask is filled with water up to three-fourths of its capacity. The cork with its fittings is then placed at the mouth of the flask and fitted tightly. The tubes are then adjusted so that the longer limb of the tube bent at acute angle reaches almost near the bottom of the flask, the inserted limb of the other tube is a little above the water-level and the two bent arms of the two tubes, kept outside the bottle, are so placed that they lie on a straight line. The wash-bottle, with fitting, should be air-tight.

*To check that the wash-bottle, so fitted, is air-tight.*— If the fittings of a wash bottle are not air-tight, the wash bottle will not work properly, since in such cases, the air blown through the shorter tube (mouth-piece) will pass out through the leak and hence, sufficient pressure will not be developed within the bottle and water will not be blown out. If it so happens, the cork must be tightened further and, if required, the glass-to cork contacts should be sealed by molten wax. If the bottle is air-tight water will come out through the jet when air is blown through the mouth-piece.

[ N. B. The use of a rubber tube for connecting the jet helps much in efficient washing of precipitates or apparatus since, being flexible, it can be turned in different directions and washing can be properly carried out. ]

## ORAL QUESTIONS

1. What is the name of the instrument which is used to scratch a glass tube before cutting it ?

2. What sort of a burner is suitable for bending glass tubes ?

3. Why should a glass tube be uniformly heated on all sides before bending ?

4. Why uniform mild pressure is to be applied on both sides of a glass tube for bending it ?

5. What is a jet ?

6. Is it possible to prepare a jet by elongating a softened glass tube on one side only ?

7. What are your considerations for choosing a suitable cork for a wash bottle ?

8. Is a cork-squeezer essential before boring a cork ?

9. Why a cork-borer is to be pressed vertically downward during boring of a cork ?

10. What are the angles at which the tubes in a wash bottle are to be bent and why ?

11. Why a small rubber tube is used for connecting a jet to the shorter limb of the longer tube in a wash bottle ?

12. What would be happen, if the jet is connected to the shorter tube of wash bottle ?

13. How could you know that the cork fitted to a wash bottle is air-tight ?

14. Will it create much inconvenience if the fitting of a bottle is not air-tight ?

## 3

# SEPARATION OF MIXTURES
## By
## Common Laboratory Processes

---

**Mixtures :** If on mixing two or more substances (elements or compounds), no chemical reaction occurs among them, but they remain in contact with one another side by side, each retaining its own characteristic properties, a substance results, which is known as a **mechanical mixture** of its components.

Thus, a mechanical mixture is a substance made up of more than one components, each of which can be identified by its own characteristic properties. So, the components of a mixture can be easily separated from each other by common laboratory processes, since they retain their characteristic properties.

It can easily be conceived that, due to the differences in properties, different methods of separation are to be adopted for separating the components of mixtures. So, it needs no mentioning that the process (or processes) for separating the components of a given mixture is to be chosen after considering the nature of the mixture, *i.e.* after throughly studying the properties of the substances to be separated.

There are several processes which are easy and commonly practised in laboratories for various types of separation whenever necessary. These processes are *filtration*, *sublimation*, *crystallisation*, *distillation*, *solvent extraction etc.*, of which any one (or more) may be chosen and used for the separation of the components of a given mixture.

### Separations involving filtration.

If the given mixture contains such substances that one of them is soluble in water or any other liquid solvent, while the others are not, then an efficient separation of that soluble substance may be made through filtration.

**Filtration.**—It is the process of separation of a liquid—a pure solvent or a solution containing dissolved substances—from the substance(s) insoluble in that liquid, with the help of a filter paper

9870

(or other filtering medium), through which only the liquid (solvent or solution) can pass but not the other substances insoluble in that liquid. It involves dissolution of the substance (*i. e.* the soluble component of the mixture) in water (or other solvent in which it is soluble, while others are not), followed by separation of the solution through a filter paper properly folded and fitted in a filtering funnel, when the insoluble substances will be retained by the filter paper and the solution will pass through the filter paper and collect in a receiver placed beneath the funnel.

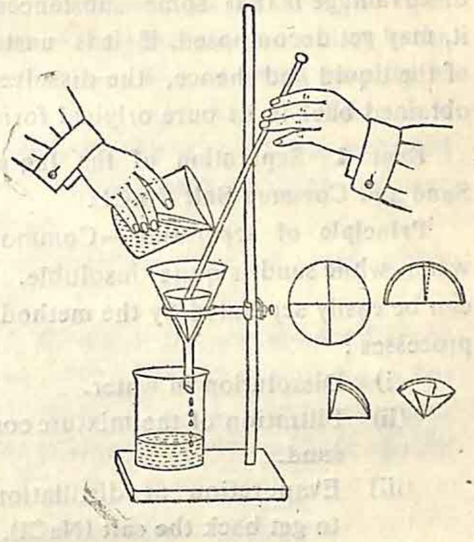


Fig. 3-1.—Filtration.

Although a component substance (soluble component) of the mixture is thus separated from others, it still remains *in solution*. To get the substance in its original solid form, it is required to adopt other processes, *e.g.* evaporation or distillation, when the liquid (solvent) will go off, leaving behind the substance in the solid state.

**Evaporation.**—It is the process of transforming a liquid (solvent or solution) into vapour, either by keeping it open to air under ordinary conditions of temperature and pressure (slow process), or by heating it just below its boiling point (rapid process). Sometimes it is required to remove a liquid from a mixture (or the solvent of a solution) more rapidly. It is then heated to its boiling point, when the liquid boils and passes rapidly into vapours. These processes are called **evaporation.**

**Distillation.**—It is the process of converting a liquid at its boiling point into vapours, followed by condensing the vapours again into the liquid state. It is a rapid process and it has the advantage over evaporation (or vaporisation) in that the liquid (solvent) can be recovered. But, its main disadvantage is that some substances, remaining dissolved in it, may get decomposed, if it is unstable at the boiling point of the liquid and hence, the dissolved substance may not be obtained back in its pure original form.

**Expt. 1 –Separation of the Ingredients of a Mixture of Sand and Common Salt (NaCl).**

**Principle of separation.**—Common salt dissolves well in water, while sand is quite insoluble. So, the two ingredients can be easily separated by the method involving the following processes :

(i) Dissolution in water.

(ii) Filtration of the mixture containing the solution and sand.

(iii) Evaporation or distillation of the filtrate (solution) to get back the salt (NaCl).

**Apparatus.**—(1) 2 beakers (2) A glass rod (3) A glass funnel, (4) Filter paper, (5) An evaporating basin, (6) A distilling flask, (7) A bored cork fitted with a delivery tube, (8) One more bored cork, (9) a conical flask. (10) A tripod stand, (11) A wire-gauze and (12) A bunsen burner.

**Procedure : (i) Dissolution of salt in water :** The given mixture is taken in a beaker and sufficient water is added. It is then stirred well with a glass rod, when almost all the salt goes into solution. If any salt is left undissolved, the mixture is warmed with stirring when all the salt will go into solution.

(ii) **Filtration :** A piece of filter paper is folded into halves and then into quadrants. It is then unfolded with three quadrants on one side and one quadrant on the other, so that a cone is formed. This is fitted to the funnel and is fixed to it by moistening with a little water. The funnel with the filter paper is placed on a ring clamped to a stand. An empty clean beaker is placed under the funnel in such a position that the stem of the funnel touches the inner wall of the beaker.

Now, the solution from the first beaker is poured on the thicker side of the filter cone down the glass rod held against the spout of the beaker. The sand is arrested by the filter paper and the common salt solution passes through and is collected in the beaker below. The sand still remaining in the first beaker is treated once more with a small quantity of water from a wash bottle and the process of filtration is repeated till the filtrate is free from the salt. (It may be tested by treating the filtrate with silver nitrate solution when no turbidity should be produced.)

Thus the sand is separated from common salt which remains in solution in water.

Note : (1) The ordinary filtration process described above works slowly and hence, the process is time-consuming. The operation can be hastened by adopting rapid filtration process. The apparatus used for this purpose consists of (i) a special type of funnel (called Buchner funnel) fitted with a porous plate acting as the filtering medium and (ii) a conical flask with a side-tube. The funnel is fitted (air-tight) to the mouth of the flask with the help of a rubber stopper, and the side-tube is connected to a water-pump by means of a pressure-tube. The mixture to be filtered is poured into the funnel after covering the filtering bed with a piece of filter paper cut exactly according to the shape and size of the porous plate. On running the pump, filtration is performed rapidly.

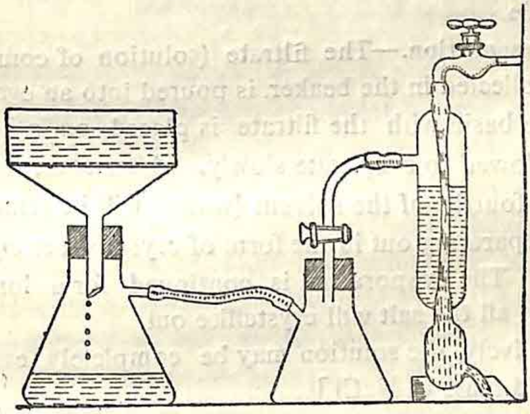


Fig. 3-2.—Rapid filtration.

(2) If it so happens that one of the components of the mixture is soluble in hot water but is insoluble in the cold,

then hot-filtration process is to be adopted, since the solution made at higher temperature will get cooled and the substances precipitated during ordinary filtration. This will be the case if a mixture of sand and $PbCl_2$ (instead of NaCl), is to be separated. $PbCl_2$ is soluble completely in hot water but it precipitates on cooling. In this case, the mixture is boiled with water, when $PbCl_2$ goes into solution. It is then filtered through a filter paper using the apparatus (shown in fig. 3-3) which is provided with heating system. The filtrate on cooling or evaporation, gives solid lead chloride.

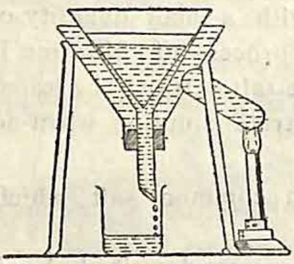


Fig. 3-3.—Hot filtration.

(iii) **Evaporation.**—The filtrate (solution of common salt in water), collected in the beaker, is poured into an evaporating basin. The basin with the filtrate is placed on a hot water bath and allowed to evaporate slowly. After some time, when about three-fourths of the solvent (water) will be removed, the salt starts separating out in the form of crystals (see *crystallisation, p. 28*). The evaporation is continued for a longer time when almost all the salt will crystallise out.

[Alternatively, the solution may be completely evaporated to get a solid mass of NaCl]

N B. (i) In such an evaporation process, it is very difficult to remove last traces of water. The mixture should then be heated slowly on a sand-bath, when last traces of water will be removed.

(2) The process of evaporation is not at all advantageous since it takes too long a time and hence unsuitable for a routine work in the laboratory Instead, the solution may be vaporised by heating the basin directly on a Bunsen flame or better by placing the basin with the solution on a sand-bath heated by Bunsen burner. It will take only a few minutes to remove all the water.

**Distillation**—The liquid (*i e.* the filtrate—a solution of common salt in water) is taken in a round-bottomed distilling flask which is placed on a tripod stand over wire-gauze and kept in position with the help of a clamp and a stand A few glass beads or small pieces of broken procelain ware are dropped in to avoid unusual bumping of the liquid during boiling. The mouth of the flask is closed by a cork fitted with a bent exit tube which is connected by means of a bored cork to one end of a Leibig condenser, the other end of which is inserted into a conical flask used as a receiver. The Leibig condenser is kept in position by means of a clamp and a stand and the inlet-side tube (towards the lower end) of the condenser is connected by means of rubber tube to a cold-water tap, while the rubber tube fitted to the other side-tube (towards the upper end of the condenser is led to the sink.*

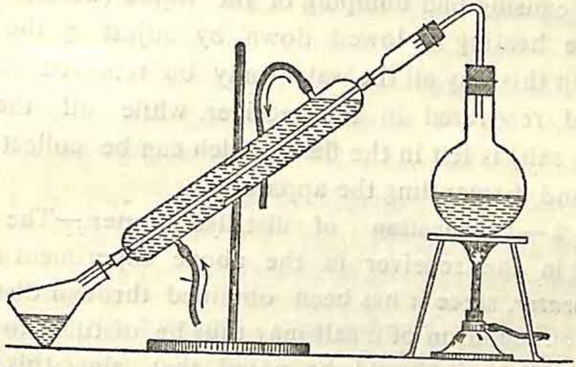


Fig. 3.4.—Distillation.

Now, the Bunsen burner, placed below the distilling flask and connected to the gas tap, is lighted on. The water tap, to which the condenser has been connected, is also turned on, when water flows through the condenser to the sink. Within a short time, the liquid will begin to boil and after a few minutes, water vapour coming out of the flask and entering into the condenser will condense again to a liquid by coming in contanct with the inner surfaces of the condenser which are kept cooled by continuously circulating cold water through the outer jacket. The water, thus produced within the condenser, passes out and collects in the receiver. Towards the end of the distillation, when more than three-fourths of the liquid (water) have come out, solid sodium chloride begins to separate, causing bad bumping of the liquid (water). At this point, the heating is slowed down by adjusting the burner-flame. In this way all the water may be removed from the flask and recovered in the receiver, while all the solid (common salt) is left in the flask, which can be collected after cooling and dismantling the apparatus.

---

*It is better to insert through the cork another tube (not shown in the figure), long enough to reach almost the bottom of the flask on one side and extend up to a certain height on the upper side. It will provide the apparatus with safety, since during rough and abrupt bumping, some liquid may go out and thus save the flask from bursting.

**Expt. 2.—Preparation of distilled water.**—The water collected in the receiver in the above experiment is called *distilled water*, since it has been obtained through distillation. An aqueous solution of a salt may thus be distilled to prepare distilled water. It should be noted that, since this water is obtained through distillation, it is obviously free from any dissolved solid matter which is not volatilised during distillation. In the laboratory, distilled water is prepared, as a routine work, by distilling impure tap water (containing dissolved salts) to which a little $KMnO_4$ has been added. Commonly, a copper flask is used for this purpose.

**Expt. 3.—Separation of the ingredients of Gun Powder.**—Gun powder is a mixture containing the following ingredients :

(i) Nitre ($KNO_3$)—Soluble in water, but insoluble in carbon disulphide.
(ii) Sulphur—Insoluble in water but soluble in carbon disulphide.
(*iii*) Charcoal powder—Insoluble in both water and carbon disulphide.

The ingredients of this mixture can be separated by the process described above. The mixture is first treated with water when only nitre goes into solution, from which the other two (charcoal and sulphur) are separated through filtration. The residue is dried and treated with carbon disulphide and shaken well, when sulphur goes into solution, from which charcoal is separated through filtration. The solutions of nitre (in water) and of sulphur (in carbon disulphide) are evaporated (and dried) to get the respective solid ingredients. Charcoal, left as the residue, may also be dried and collected.

### Separation of the Ingredients of a Mixture through Sublimation.

**Sublimation**.—There are certain substances which, when heated, directly pass into vapour without being converted to the liquid state, *e g*. camphor, iodine, naphthalene *etc.* If these substances are heated, they directly pass into vapour and if the vapours are cooled, the original substances are obtained in the solid state. This process of converting a solid substance directly into vapour and re-conversion of the vapour to the solid state again through condensation is known as **sublimation.**

If a mixture contains a substance that can be easily sublimed, then the easiest process of separating such a substance from the other ingredients of the mixture is sublimation.

**Expt. 4—To separate a mixture of sand and Iodine** (or **Camphor**).

**Principle of separation.**—Of the two ingredients of the mixture, only iodine (or camphor) can be sublimed, but not the sand. Therefore, it is possible to separate sand from iodine (or camphor) by the process of sublimation.

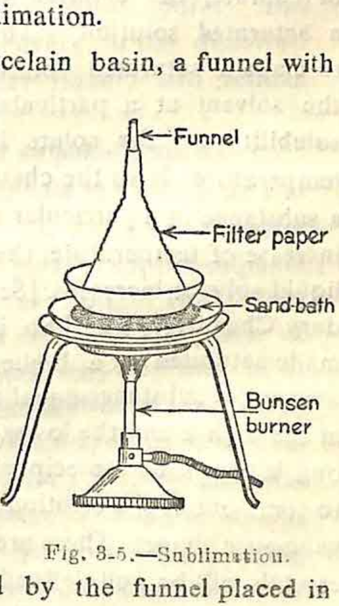


Fig. 3-5.—Sublimation.

**Apparatus**.—An evaporating porcelain basin, a funnel with a long stem and wide mouth, a few pieces of blotting paper, a mortar and a pestle, a tripod stand, a sand-bath and a Bunsen burner.

**Procedure.**—The given mixture of sand and iodine (or camphor) is taken in the mortar and thoroughly mixed with the help of the pestle. The mixture is then transferred to the evaporating basin which is placed on the sand-bath over the tripod stand. The mixture in the basin is covered by the funnel placed in inverted position, the outer surfaces and the stem of which are wrapped with filter paper soaked in water. Now the basin with the mixture is warmed slowly by heating the sand-bath with Bunsen burner placed below the bath. Iodine (or camphor) will sublime and collect on the cooled inner surfaces of the funnel in the form of small violet crystals (or white crystals in the case of camphor). After some time, when sublimation is supposed to be camplete, the burner is put off, the basin is taken out of the sand-bath and allowed to cool. The funnel is then taken out and the iodine (or camphor) is collected by scraping the inner surfaces of the funnel

### Separation of the Ingredients of a Mixture through Crystallisation.

#### Crystallisation : Fractional crystallisation

Dissolution of a substance in a solvent depends upon the nature of both the solvent and the soulte. At the same time, the amount of a solute that can be dissolved in a definite volume of a solvent also depends upon the nature of the both and also on the temperature. When a given volume of a solvent at a particular temperature dissolves the maximum amount of a solute, the solution that will be obtained is known as a **saturated** solution. The amount of substance required to make a saturated solution, when dissolved in 100 gms. of the solvent at a particular temperature, is known as the **solubility** of the solute in that solvent at that particular temperature. With the change of temperature, the solubility of a substance in a particular solvent changes. Generally, with increase of temperature, the solubility of a solid substance in a liquid solvent increases. [See Poddar & Haldar : Higher Secondary Chemistry, § 33.] So, it is an easy guess that, if a solution, made saturated at a higher temperature, is cooled down, an amount of substance equal to the difference in its solubilities at the higher and the lower temperatures will be precipitated out. Where such a precipitation occurs, the substance is found to come out of the solution in small solid particles with definite geometric shapes. These are called **crystals**. The shapes of the crystals will be well-defined, if cooling is done slowly. This process of separating a solid substance from the solution in a liquid solvent in the form of crystals is called **crystallisation.**

Thus, crystallisation is a process which can be adopted in separating dissolved solids from a solution, and it depends upon the change in solubility of the substance with the change in temperature.

It may be noted that the dissolved substance may also be precipitated out, if a solution is evaporated to reduce the volume of the solvent, and then cooling the resulting solution, since less amount of the solvent left would then be able to keep less amount of the solute dissolved in it, and hence, the excess amount of the solute would get precipitated. If, say, a saturated solution consisting of 100 gms. of water and W gms. of a substance X at ordinary temperature is evaporated to half its volume (50 ml) and then cooled to room temperature then obviously, $\frac{W}{2}$ gms. of X will be precipitated in the form of crystals. If the precipitated substance is separated by filtration and the filtrate is evaporated again, then similarly, another lot of crystals of X will be obtained and thus, the substance X can be recovered in the form of crystals.

Through crystallisation process, then, substances can be obtained in the crystalline form and hence, pure. But this process does not allow the full recovery of the dissolved substance, since the last filtrate (mother liquor) still retains some solid in the dissolved state.

**Expt.-6.—Crystallisation of Copper sulphate from water.**

**Principle.**—Solubility of copper sulphate in water is 20·7 at 20°C, 40 at 60°C and 55 at 80°C, *i.e.* 100 gms. of water would get saturated by dissolving 20·7 gms. of copper sulphate at 20°C, 40 gms. at 60°C and 55 gms. at 80°C. Thus, if to 50 gms. of copper sulphate are added 100 gms. of water at room temperature (20°C) and stirred well, only 20·7 gms, of it will dissolve and the rest will remain undissolved at the bottom of the vessel. If, however, this mixture is heated to 80°C, then all the copper sulphate will go into solution, leaving no solid residue, since solubility of copper sulphate in water at 80°C is 55. Now, if we allow the solution to cool down slowly again to room temperature, it will be observed that an amount of copper sulphate (about, 50 – 20 = 30 gms.) has been separated in the form of beautiful blue crystals.

**Apparatus.**—Two beakers of 250 ml. capacity, a glass rod, a mortar and a pestle, a measuring cylinder, a Bunsen burner, a wire-gauze, a tripod stand, a funnel, filtering stand and filter paper, and a rough balance.

**Materials** required are water and copper sulphate.

**Procedure.**—About 25 gms. of solid copper sulphate are weighed and taken in the mortar. It is then finely ground with the help of the pestle. The ground mass is transferred to a beaker. About 50 gms. (roughly, 50 ml., measured out by the measuring cylinder) of water are added to it and stirred well with a glass rod; when a part of copper sulphate will dissolve, imparting a blue colour to the solution, the rest remaining undissolved. The beaker with the mixture is then placed on the wire-gauze over a tripod stand and heated by the Bunsen burner with constant stirring by means of a glass rod. With the rise in temperature, more copper sulphate will be observed to go into solution and soon the whole of the copper sulphate will dissolve, when the solution will be hot enough to vapourise rapidly. Heating is continued even after the solution starts boiling to reduce the volume to some extent.

When the volume of the solution is reduced to about 25 ml., heating is stopped; the beaker with the mixture is kept in a cool place on the table and allowed to cool down slowly. Within a short time, crystals of copper sulphate will start separating out, and it will be completed within an hour or two (It is better to keep it overnight.) The crystals are then collected through filtration with the filter paper, washed on the filter paper with a little water and then with alcohol and dried by pressing between dry filter papers.

**Note :** Similar experiments on crystallisation may be performed with other substances like NaCl, $KNO_3$, sugar, alums *etc.*, using water as solvent.

**Fractional crystallisation.**—When two (or more) substances present in a mixture are soluble in a common solvent (but neither of them is sublimable), and their solubilities in that solvent differ appreciably, then one component may be separated by crystallisation in preference to the others. Such a crystallisation process is called *fractional crystallisation.*

## Separation of the Ingredients of a Mtxture by Fractional Crystallisation.

**Expt.-7.—To separate sodium chloride from sodium nitrate present in a mixture.**

**Principle and Procedure.**—Both sodium chloride and sodium nitrate are soluble in water and neither of them is sublimable. So, from a mixture, they can be separated through fractional crystallisation, since solubility of sodium chloride in water (35·85 at 18°C) differs considerably from that of sodium nitrate (83·97 at 18°C) in the same solvent.

The given mixture is, therefore, to be dissolved in sufficient water. The solution is subjected to evaporation to reduce its volume appreciably.

The resulting solution, on cooling, will deposit either pure sodium chloride crystals or a mixture consisting mainly of sodium chloride and a little sodium nitrate, since the solubility of sodium chloride is much less than that of sodium nitrate. Several such processes will give pure sodium chloride, free from sodium nitrate. Thus, sodium nitrate will remain in solution (filtrates or mother liquors) of several repeated crystallisations, which may be collected together and evaporated to a small volume to get crystals of pure sodium nitrate.

**Expt.-8.—Separation of sodium chloride from magnesium sulphate in a mixture.**

A mixture of NaCl (say 10 gms.) and $MgSO_4$ (say 2 gms.) was taken and was dissolved in sufficient quantity of water. The solution is then heated to evaporate off water until the volume is reduced to 10 ml. The solution is then allowed to cool to 35°C* [ measured with a thermometer, the bulb of which is kept dipped into the solution ], when almost all (6-7 gms.) of pure NaCl will crystallise out, leaving only 3-4 gms. NaCl and all of the $MgSO_4$ in solution. The solution is then further evaporated to 5 ml. and on cooling it to 35°C, a further crop of NaCl will be obtained, which will be contaminated with some $MgSO_4$. This crop of precipitate and also the filtrate may be again subjected to fractional crystallisation as described above, to separate the components of the mixture.

---

* On cooling below 30°C, $Na_2SO_4 . 10H_2O$ will crystallise out and $MgSO_4$ cannot be obtained back at all.

The above is not a satisfactory method for the given separation. The mixture is best separated by passing HCl gas through the solution (10 ml.) at 35°C, when practically all NaCl will be precipitated. This is filtered and the filtrate, on evaporation, gives practically pure $MgSO_4$.

**Note :** This process of factional crystallisation may be used to separate such mixtures as KCl (32·95) and KBr (65·85) ; $CaCl_2$ (73·19) and $BaCl_2$ (37·24) etc. [ The figures in the parentheses are their respective solubilities at 18°C.]

### Separation of the components of a liquid mixture.

Liquid mixtures may be of two types : (i) *heterogeneous*—in which the components are immiscible and hence, are present in separate layers, *e.g.* ether-water mixture, and (ii) *homogeneous*—in which the components are miscible and hence, form a homogeneous solution, *e.g.* alcohol-water mixture.

The liquid mixtures of type (i) can be separated into their components easily with the help of a separating funnel, by allowing the lower heavier liquid layer to pass through the stop-cock (turned on) first and then the upper lighter liquid layer.

To Separate the components of a liquid mixture of type (ii), fractional distillation process should be resorted to [vide Poddar & Haldar, Higher Secondary Chemistry, vol. I,p. xiii].

**Method of Solvent Extraction.**—This is a good process to separate without precipitations, solids present in a solution, by means of a solvent immiscible with the solvent of the solution. A liquid (solvent) is chosen in which the component to be separated is more soluble than in the solvent of the solution in which it is present. The given solution is shaken vigorously in a separating funnel with the

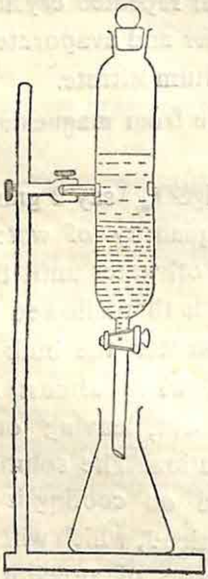


Fig. 3-6. Apparatus or solvent extraction.

chosen solvent to extract the required compotent from the solution into the new solvent. If now the mixture is allowed to stand, then two distinct layers will be formed, which are separated and collected one after another and the solute is recovered by evaporating off the solvent. If a solution of iodine in water is given, then the dissolved iodine can be separated easily by shaking the solution with chloroform or carbon tetrachloride (in which iodine is much more soluble than in water), separating the two layers. Solid iodine may be collected by evaporating off the chloroform or $CCl_4$-layer (violet).

## ORAL QUESTIONS

1. What is a mixture ?

2. Suggest the process you would adopt to separate the ingredients of the following mixtures :

    (i) Sugar and common salt.
    (ii) Carbon disulphide and water.
    (iiij Charcoal and iodine.
    [Hint : Iodine is soluble in chloroform].
    (iv) Copper sulphate and sodium chloride.
    (v) Camphor, sodium nitrate and silver chloride.
    [Hint : Silver chloride is insoluble in water.]
    (vi) Lead chloride and calcium chloride.

3. What is distilled water ? Is it *pure* water ?

4. What is crystalisation ? How does it differ from fractional crystallisation ?

# 4

# PREPARATION OF GASES
## And
## Studies of their properties.

## *1. HYDROGEN

**Principle of preparation.**—In the laboratory, hydrogen is prepared by the action of dilute sulphuric (or hydrochloric) acid on granulated commercial zinc*:

$$Zn + H_2SO_4 = ZnSO_4 + H_2\uparrow \; ; \; Zn + 2HCl = ZnCl_2 + H_2\uparrow$$

*(i) Dilute mineral acids do not readily act on pure zinc and hence, evolution of hydrogen takes time and the rate is slow, while they readily react with commercial zinc, which is impure, containing traces of other metals. If, however, pure zinc granules are used, it is advised to add a few drops of copper sulphate solution, when a layer of metallic copper will be deposited on zinc, forming zinc-copper couple, which readily reacts with dil. acids.

(ii) Instead of zinc, other metals like Mg, Fe etc. may also be used for the preparation of hydrogen.

**Apparatus.**—(i) A Woulf's bottle (or a flat-bottomed flask of 1 liter or 500 ml. capacity; (ii) A thistle funnel, (iii) A delivery tube, (iv) Two corks with single bore (or one cork with double bore), (v) Gas jars with lids, (vi) A pneumatic trough, (vii) A beehive shelf, (viii) Tapers, (ix) Bunsen burner *etc.*

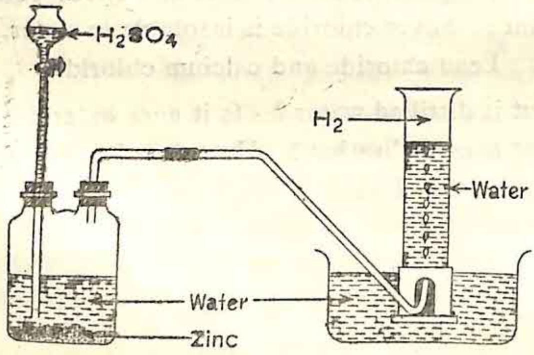


Fig. 4-1. Preparation of hydrogen in the laboratory.

**Chemicals required.**—(i) Granulated commercial zinc, (ii) Dilute sulphuric (or hydrochloric) acid, (iii) copper sulphate solution, (iv) Potassium permanganate solution and (v) Blue and red litmus papers.

**Procedure.**—(i) The Woulf's bottle is washed with water and some pieces of granulated zinc are taken in it.

(ii) The two mouths of the Woulf's bottle are fitted with two single-bored corks, through one of which is inserted a thistle funnel, the end of which reaches almost the bottom of the bottle, and through the other, a delivery tube.

(iii) The apparatus is to be checked to see that the fittings are air-tight. To do this, some water is poured into the bottle through the thistle funnel (the lower end of the funnel must remain dipped into water) and air is blown (by mouth) into the bottle through the delivery tube, when water would rise through the stem of the thistle funnel. The end of the delivery tube is closed with a thumb and it is observed whether the level of water stands stationary in the stem of the thistle funnel. If it is so, the apparatus is considered to be air-tight. Otherwise, the fittings are to be tightly done (or the glass-to-cork connections should be sealed with wax) until the apparatus becomes air-tight.

(iv) The pneumatic trough is filled with water, the bee-hive shelf is placed in the middle of it under water and the outer end of the delivery tube is introduced into the opening of the bee-hive shelf.

(v) Dilute sulphuric acid is poured down the thistle funnel into the bottle, along with about 0·5 ml. of $CuSO_4$ solution. The acid would come in contact with the granulated zinc and hydrogen gas will be liberated, which would escape along the delivery tube and bubble through water.

(vi) The gas is allowed to escape for some time to sweep out all the air from inside the apparatus.

(vii) A gas jar is now filled with water and placed upside down on the bee-hive shelf. Hydrogen gas collects in the jar by the downward displacement of water.

A few more gas-jars are filled similarly with hydrogen, closed with proper lids and stored for the study of its properties.

**Study of the properties of Hydrogen.**—For the study of the properties of hydrogen, the following experiments are performed and the observations with inferences are noted, as shown below :

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. The colour of the gas is observed and by opening the lid of the gas-jar, the gas is smelt. | No colour, no odour. | Hydrogen is a colourless, odourless gas. |
| 2. A lighted taper is introduced into a jar containing hydrogen. | The taper is extinguished while the gas itself burns at the mouth of the jar with a blue flame. | Hydrogen is not a supporter of combustion, but is itself combustible. It burns in air with a blue flame. |
| 3. A gas-jar, filled with hydrogen is kept under another inverted bigger jar and the gas is lighted as in experiment (2). After the burning of the gas, the bigger jar is examined. | The gas burns with a blue flame and the inner surface of the bigger jar is found to contain drops of water. | During combustion of hydrogen in air, water is produced through its combination with oxygen : $2H_2+O_2=2H_2O$. |
| 4. A jar, full of air, is held inverted on the mouth of a jar full of hydrogen and the lid is removed. After a few seconds, both the jars are tested with a lighted taper as in experiment (2). | (i) The gas in the upper jar immediately catches fire with a bursting sound and burns with a blue flame and the taper extinguishes, proving that it contains hydrogen.<br>(ii) The gas in the lower jar does not burn, proving that it is air. | Hydrogen is lighter than air, and that is why it comes up from the lower jar to the upper one by replacing air, which then fills the lower jar.<br>The bursting sound produced during lighting is due to the fact that hydrogen produces an explosive mixture with oxygen (air). |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 5. The gas is tested with wet litmus papers—first with red litmus paper and then with blue litmus paper. | None of the litmus papers changes its colour. | Hydrogen is neither acidic nor basic in nature ; it is a neutral gas. |
| 6. (i) The gas is passed through dilute aqueous potassium permanganate solution taken in a test tube*. | (i) The permanganate (pink colour) solution retains its colour. | Molecular hydrogen does not reduce $KMnO_4$ soln. |
| (ii) In another test tube, half-filled with the same permanganate solution, are added a few pieces of granulated zinc and a little dilute sulphuric acid. | (ii) The pink colour of the permanganate is destroyed and it becomes colourless. | Nascent hydrogen is a stronger reducing agent and reduces potassium permanganate solution. |

*The gas produced in the Woulf's bottle should be directly used.

**Precautions**—(i) The apparatus must be air-tight.

(ii) The lower-end of the thistle funnel must remain dipped in the acid-water mixture within the Woulf's bottle.

(iii) Air within the Woulf's bottle must be removed before collecting the gas in gas-jars, otherwise the collected gas will explode violently on ignition.

(iv) Lighted burners must be removed from the place of experiment.

## *2. OXYGEN

**Principle of preparation.**—In the laboratory, oxygen is prepared by heating a mixture of potassium chlorate ($KClO_3$) and manganese dioxide ($MnO_2$)* in the weight-ratio 4 : 1.

$$2KClO_3+[MnO_2]\xrightarrow{360^\circ C}2KCl+3O_2\uparrow[MnO_2].$$

*In this reaction, $MnO_2$ acts as a catalyst. It does not take part in the reaction, but helps the reaction run smoothly at lower temperature. In fact, on heating $KClO_3$ alone, it would produce oxygen, but it requires higher temperatures, at which $KClO_3$ tends to explode.

**Apparatus.**—(i) A hard-glass test tube, (ii) A single-bored cork which fits into the test tube, (iii) A delivery tube bent at an obtuse angle, which fits into the bore of the cork, (iv An iron stand with a clamp, (v) A pneumatic trough, (vi) A bee-hive shelf, (vii) Gas jars with lids, (viii) A deflagrating spoon, (ix) A Bunsen burner, (x) A taper and a piece of charcoal and (xi) A mortar with a pestle.

**Chemicals required.**—(i) Potassium chlorate ($KClO_3$), (ii) Manganese dioxide ($MnO_2$) (*note—1*), (iii) Sulphur, (iv) Metallic sodium, (v) Lime water, (vi) Blue and red litmus papers.

**Procedure.**—(i) Potassium chlorate (4 parts by weight) and manganese dioxide (1 part by weight) are taken together in a mortar and mixed intimately with the pestle. The mixture is then taken in the test tube in such an amount that the tube is just half-filled. The test tube is fitted with the bored cork, through which passes the delivery tube protruding upto a little inside the test tube.

(ii) The test tube is then fixed to the iron stand by a clamp, with its mouth slightly inclined downwards.

(iii) The pneumatic trough, with the bee-hive shelf placed in its middle, is filled with water and the outer end of the delivery tube is introduced inside the opening of the bee-hive shelf.

(iv) The mixture is now heated with the Bunsen flame, *at first gently, with slow motion of the flame from the middle owards the bottom of the test tube.*

(v) Oxygen begins to evolve. The gas is allowed to escape for some time to sweep out air completely from the tube.

(vi) A gas-jar is now filled up with water and placed upside down over the bee-hive shelf, when oxygen will be collected in it by downward displacement of water.

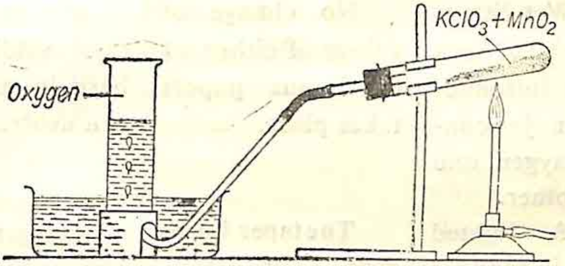


Fig. 4-2. Preparation of oxygen in the laboratory.

(vii) A few more jars are similarly filled up with oxygen, closed with lids and stored for performing the experiments described below.

---

*Note-1.* Manganese dioxide must be free from charcoal powder, with which it is often contaminated, since carbon forms an explosive mixture with potassium chlorate, and serious explosion may occur during heating the mixture. To test for the purity of $MnO_2$, it is *always advisable* to heat a *very small quantity* of the prepared mixture of $KClO_3$ and $MnO_2$ in a test tube before carrying out the actual experiment. If no explosion takes place during heating this sample, the actual experiment with a larger quantity may be done.

*2.* After the collection of the gas, the delivery tube should be removed from the pneumatic trough before the heating is stopped ; otherwise, water from the trough may be sucked back into the hot tube, causing violent explosion.

---

**Study of the properties of oxygen :** To study the properties of oxygen, the following experiments are performed with the gas.

prepared and the observations with inferences in each case are taken down as below :

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. The colour of gas is noted and its odour examined. | No colour, no odour. | Oxygen is a colourless as well as odourless gas. |
| 2. Wet litmus papers—blue and red—are introduced into a jar containing oxygen, one after another. | No change of colour of either of the litmus papers takes place. | Oxygen is neither acidic not basic in nature ; it is a neutral gas. |
| 3. A lighted taper is introduced inside a jar of oxygen. | The taper burns more brilliantly, but the gas does not catch fire. | Oxygen is a supporter of combustion, but it is not combustible. |
| 4. (*a*) A piece of charcoal is taken in a deflagrating spoon and heated until it glows. The spoon with the glowing charcoal is then introduced into a jar of oxygen. | The glowing charcoal burns brilliantly. | Oxygen is a good supporter of combustion and carbon burns in oxygen forming carbon dioxide : $C+O_2=CO_2$. |
| (*b*) Lime water is poured into this jar ; the mouth of the jar is closed with the lid and shaken thoroughly. | The lime water turns milky. | The gas produced by the burning of charcoal in oxygen is carbon dioxide, which reacts with $Ca(OH)_2$(lime water), forming $CaCO_3$, and so the lime water appears milky. $Ca(OH)_2+CO_2$ $=CaCO_3+H_2O$. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 5 (*a*) Experiment 4(*a*) is repeated by taking sulphur (instead of charcoal) in the deflagrating spoon. | Sulphur burns brilliantly in oxygen ; fumes with peculiar pungent smell (smell of burnt sulphur) are produced. | Sulphur burns in oxygen, forming sulphur dioxide which produces white fumes and smells like burnt sulphur. |
| (*b*) A wet piece of blue litmus paper in introduced in this jar. | The paper turns red. | Sulphur dioxide is an acidic oxide ; it forms sulphurous acid with water which turns blue litmus paper red. $SO_2+H_2O=H_2SO_3$. |
| 6. The experiment 4(*a*) is repeated with a piece of metallic sodium (instead of charcoal). | Sodium burns with a bright yellow flame and a white residue is left. | Sodium readily reacts with oxygen, forming sodium oxide : $4Na+O_2=2Na_2O$ |
| (*b*) Water is poured into the jar and shaken, and then a red litmus paper is introduced into the solution. | The residue dissolves in water and the solution, thus produced, turns red litmus paper blue. | Sodium oxide dissolves in water, forming sodium hydroxide which is alkaline and hence, it turns red litmus paper blue : $Na_2O+H_2O$ $=2NaOH$ |

**Precautions.**—(i) Carbon-free manganese dioxide must be used.

(ii) The hard-glass tube must be fixed to the stand with its mouth slightly inclined downwards,[*] and heating of the mixture must be done very gently at the beginning.[†]

---

[*] This is to be done to avoid breaking of the tube. On heating the reaction mixture, water vapours are produced which condense in the cooler part near the mouth. If the tube is set slanting towards the bottom which is hotter, the bottom part of the tube would crack.

[†] This is to be done to avoid too rapid evolution of gas which may create sufficiently high pressure suddenly and thus causing explosion.

(iii) Care must be taken so that water is not sucked back from the pneumatic trough to the hot reaction-tube.

## 3. CARBON DIOXIDE ($CO_2$).

**Principle of preparation.**—In the laboratory, carbon dioxide is prepared by the action of dilute hydrochloric acid on calium carbonate (marble) :

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

**Apparatus.**—(i) A Woulf's bottle, (ii) A thistle funnel, iii) A delivery tube—doubly bent at right angles, (iv) Gas jars with lids, (v) A Bunsen burner, (vi) A pair of tongs, (vii) A taper; (viii) A candle and (ix) Some test tubes.

**Chemicals required.**—(i) Marble chips, (ii) Dilute hydrochloric acid, (iii) Lime water; (iv) Blue litmus paper, (v) A piece of magnesium ribbon.

**Procedure.**—(i) The Woulf's bottle is washed clean and a few small pieces of marble ($CaCO_3$) are introduced in it.

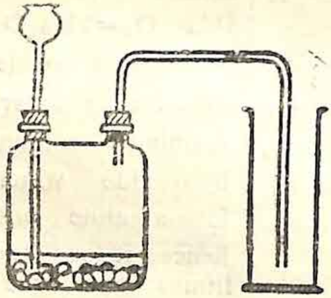


Fig. 4-3. Preparation of carbon dioxide in the laboratory.

(ii) The mouths of the bottle are fitted with bored corks, through one of which is introduced a delivery tube and through the other a thistle funnel, the lower end of which reaches almost the bottom of the bottle.

(iii) Some quantity of water is added through the thistle funnel, covering the marble chips as well as the lower end of the thistle funnel. Now, the fittings are tested to see whether they are air-tight or not, in the same way as described in the prepration of hydrogen (p. 35).

(iv) The outer-end of the delivery tube is introduced inside an empty gas-jar, placed upright, and sufficient amount of dilute hydrochloric acid (*note-1*) in added through the thistle funnel.

(v) Chemical reaction takes place immediately between marble and hydrochloric acid, producing carbon dioxide, which comes out through the delivery tube and collects in the gas jar by upward displacement of air (since carbon dioxide is heavier than air). *(note-2)*

(vi) To test whether the jar is full of the gas, a lighted taper is held at its mouth ; if the flame is extinguished, the jar is taken to be completely filled up. The mouth of the jar is then covered with a lid and is removed. In this way, a few more jars are filled up with carbon dioxide and stored for studying the properties of the gas.

*Note-1.* **Use of dil. $H_2SO_4$ for the production of carbon dioxide.**—Dilute $H_2SO_4$ is not used in conjunction with marble for the production of carbon dioxide. Dil. $H_2SO_4$ reacts first with marble, producing $CO_2$ and calcium sulphate :

$$CaCO_3 + H_2SO_4 = CaSO_4 + CO_2 + H_2O.$$

Calcium sulphate, being very little soluble in water, gets precipitated upon the marble chips and thus the reacting surfaces of the chips are gradually covered by an insoluble coating of calcium sulphate. So, after a short time, the reaction is stopped, since the contact between marble and the acid is prevented.

*Note-2.* **Collection of $CO_2$ by water-displacement.**—Carbon dioxide is appreciably soluble in water and so, if it is attempted to collect the gas by downward displacement of water, as is done in the collection of other gases, *e.g.* oxygen (p. 39), hydrogen (p. 35) *etc.*, it will be first absorbed by water, and only after the saturation of water with carbon dioxide, the gas will be collected inside the jar by displacement (downward) of water. So, a good amount of carbon dioxide will be lost. Secondly, there is the possibility of the back-suction of water into the bottle (by creation of partial vacuum due to the dissolution of the gas in water) and the whole experiment will be spoilt. For these reasons, it is not collected by water-displacement.

**Production of carbon dioxide in a Kipp's apparatus.**

Some times, a continuous or intermittent flow of a large amount of carbon dioxide is required for performing certain reactions in the laboratory. To get such a supply of carbon dioxide, it is advisable to use a Kipp's apparatus (see, $H_2S$ preparation) with marble chips and dil. hydrochloric acid.

**Study of the properties of carbon dioxide.**—To study the properties of $CO_2$, the following experiments are performed with the gas prepared and collected, and the observations with inferences are noted :

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. (*a*) A jar of carbon dioxide is examined to observe its colour and to get its smell. | No Colour, but with a mild characteristic odour. | The gas is colourless, but has a mild characteristic smell. |
| (*b*) A jar of carbon dioxide is held inverted over a jar of air. After some time, a little lime water is added to the lower jar and shaken with its mouth covered with a lid. | Lime water turns milky. | Carbon dioxide is heavier than air and goes down from the upper (inverted) jar to the lower one, where lime water turns milky. [see expt. 4 (*a*)]. |
| 2. (*a*) A lighted taper is introduced inside a jar full of $CO_2$. | The taper flame is extinguished and the gas itself does not catch fire also. | The gas is neither combustible nor a supporter of combustion. |
| (*b*) A jar of $CO_2$ is held inverted over a candle flame. | The flame is extinguished. | In $CO_2$, no combustion can take place (except in certain special cases, see expt.-3), and for that reason, when $CO_2$ is poured down on the candle flame, it goes off. |
| 3. A magnesium ribbon is lighted and it is then | The ribbon continues to burn more brilliantly with a | Metallic magnesium reacts at high temperature with |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| introduced inside a jar full of $CO_2$. | cracking sound, when black particles of carbon are deposited inside the jar and a white residue (magnesium oxide) collects at the bottom. | $CO_2$, producing magnesium oxide (MgO) and carbon (C) :<br>$2Mg + CO_2 = 2MgO + C$.<br>N.B. It is not, however, a pure case of combustion but a type of chemical reaction. |
| 4. (*a*) Some quantity of lime water is added to a jar of CO)$_2$ and the jar is well-shaken after covering with a lid. | Lime water turns milky. | Lime water contains $Ca(OH)_2$ which reacts with $CO_2$, forming insoluble $CaCO_3$: $Ca(OHl_2) + CO_2 = CaCO_3 + H_2O$. It is due to this insoluble $CaCO_3$ that the lime water appears to be milky. |
| (*b*) Through the milky lime water produced in expt. 4(*a*) is passed more $CO_2$ from the Woulf's bottle for some time. | Milky lime water again turns clear. | The suspended $CaCO_3$ in milky lime water reacts with more $CO_2$, forming soluble calcium bi carbonate $CaCO_3 + CO_2 + H_2O = Ca(HCO_2)_2)$; since $Ca HCO_3 {}_2$ is soluble in water, milkiness disappears and thus, solution becomes clear. |
| (*c*) The clear solution obtained in expt 4(*b*) is boiled for some time. | The solution again turns milky. | Calcium bicarbonate, on heating, breaks up into $CaCO_3$ and $CO_2$ again : $Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O$. During heating $CO_2$ goes off and hence, insoluble $CaCO_3$ impartsa a milky appearance to the solution. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 5 (*a*) A jar of $CO_2$ is placed inverted over a small trough of water. | If sufficient time is allowed, water is forced to enter into the jar and the height of water inside the jar increases with time. | Carbon dioxide is moderately soluble in water. |
| (*b*) A little blue litmus solution is added to the water in the trough of the expt. 5(*a*) [or a little blue litmus solution is added to a jar of $CO_2$ and shaken after covering the mouth with its lid ] | The blue litmus solution turns red. | Carbon dioxide is ācidic in nature ; it forms an acid (carbonic acid) when dissolved in water :<br>$CO_2 + H_2O = H_2CO_3$. |
| 6. A jar of $CO_2$ is placed inverted over a small trough containing strong aqueous solution of caustic potash (or caustic soda). | Alkali solution rapidly goes up into the jar. | Carbon dioxide is an acidic oxide and so it reacts with caustic alkalis, forming alkali carbonates :<br>$2KOH + CO_2 = K_2CO_3 + H_2O$.<br>$2NaOH + CO_2 = Na_2CO_3 + H_2O$.<br>The vacuum caused by the dissolution of $CO_2$ is responsible for the entry of alkali solutions into the jar. |

**Precautions.**—(i) The apparatus should be checked to make sure that it is air-tight.

(ii) The lower end of the thistle funnel should be kept dipped into liquid.

(iii) The outer end of the delivery tube should reach almost the bottom of the jar.

(iv) Marbles should be freshly broken and washed.

---

## 4. AMMONIA ($NH_3$)

**Principle of preparation.**—Ammonia is prepared in the laboratory by heating a mixture of ammonium chloride ($NH_4Cl$) and quicklime ($CaO$) or slaked lime [$Ca(OH)_2$] ;

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O.$$

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

**Apparatus.**—(i) A hard-glass test tube, (ii) A single-bored cork, (iii) A delivery tube bent at a right angle, (iv) An iron stand with clamps, (v) Gas jars with lids, (vi) A Bunsen burner, (vii) A few test tubes and a test tube fitted with a bored cork through which a jet can be introduced.

**Chemicals required.**—(*i*) Ammonium chloride, (ii) Quicklime and aqueous solutions of the following reagents : red litmus, copper sulphate, zinc sulphate, silver nitrate, ferric chloride, aluminium sulphate, magnesium sulphate and Nessler's reagent.

**Procedure.**—(i) A quantity of dry ammonium chloride is mixed intimately with four times its weight of dry quicklime and the mixture is taken in the hard-glass test tube, so that the tube is only half-filled.

(ii) The mouth of the tube is closed by the bored crok through which is introduced the bent delivery tube (only a small portion should be introduced inside the test tube). The test tube is now fixed to the stand with the help of the clamp in a position such that its mouth is inclined slightly downwards (to prevent the back-flow of condensed water vapour produced during the reaction).

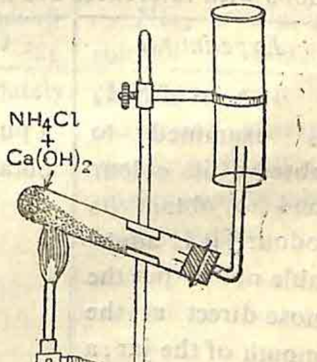


Fig. 4-4. Preparation of ammonia in the laboratory.

(iii) The outer end of the delivery tube is turned upwards and introduced deep inside an inverted, empty, dry gas jar placed above it and kept fixed by means of a clamp.

(iv) Now, the reaction-mixture within the tube is heated carefully along the length of the tube with a low Bunsen flame. The flame is gradually increased and the heating is done more strongly.

(v) Ammonia evolves and comes out through the delivery tube to the gas jar, where it collects by the downward displacement of air. ($NH_3$ is lighter than air.)

(vi) To test whether the jar has been filled up with ammonia or not, a glass rod moistened with conc HCl is held at its mouth , if dense fumes (produced by the reaction between HCl and the ammonia, coming out of the gas jar) are produced, then the jar is taken to be completely filled up with ammonia. The jar is then covered with a lid, removed and placed on the table in an inverted position. In this way, a few more jars are filled up with ammonia and stored for performing the experiments.

**Study of the properties of Ammonia.**—To study the properties of ammonia, the following experiments are performed with the gas prepared and stored as above, and the observations with inferences are noted :

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. A jar of $NH_3$ is examined to observe its colour and to obtain its odour. [It is advisable not to put the nose direct at the mouth of the jar ; a thumb may be placed inside the jar and the thumb should be smelt after taking it out ] | No colour, but a pungent smell is obtained. | The gas is colorless, but it has a pungent smell. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 2. A lighted taper is introduced inside a jar of $NH_3$ gas. | The taper is extinguished and the gas does not burn. | $NH_3$ is neither combustible nor a supporter of combustion. |
| 3 (*a*) A glass rod, moistened with conc. HCl, is introduced inside a jar of ammonia. | Dense white fumes are produced. | $NH_3$ reacts with HCl, forming $NH_4Cl$ (solid) which appears in the form of dense white fumes :<br>$NH_3 + HCl = NH_4Cl$. |
| (*b*) The inner surface of an empty gas jar is smeared with a little conc. HCl and held inverted over a jar of $NH_3$ placed upright and covered with a lid. The lid is now removed. | The upper jar becomes immediately filled with dense white fumes. | $NH_3$ is lighter than air and thus, it comes up readily and occupies the upper jar by displacing air and dense white fumes are produced by the reaction between $NH_3$ and HCl. |
| 4. (*a*) A jar of $NH_3$, covered with a lid, is held inverted over a small trough of water and the lid is removed. | Water comes up and fills the jar almost immediately. | $NH_3$ is highly soluble in water, causing a vacuum in the jar, and so, water rushes in to fill up the evacuated space inside the jar. |
| (*b*) With the solution of $NH_3$ in water thus produced (or made by dissolving sufficient amount of the gas in water) the following experiments are performed : | | |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| (i) A little red litmus solution is added to a part of the solution. | Red litmus turns blue. | The solution of $NH_3$ in water is alkaline; it contains ammonium hydroxide :<br>$NH_3 + H_2O = NH_4OH$. |
| (ii) A little of the ammonia solution is added to a solution of copper sulphate taken in a test tube. | A bluish white precipitate is formed. | The bluish white ppt. is of basic copper sulphate :<br>$2CuSO_4 + 2NH_4OH = Cu(OH)_2, CuSO_4 + (NH_4)_2SO_4$. |
| An excess of ammonia solution is added to the mixture. | The precipitate dissolves and a deep blue solution is produced. | With excess ammonium hydroxide, the basic copper sulphate dissolves, forming cuprammonium sulphate, due to which the deep blue colour develops :<br>$CuSO_4, Cu\ OH)_2 + (NH_4)_2SO_4 + 6NH_4OH = 2[Cu(NH_3)_4]SO_4 + 8H_2O$. |
| (iii) To a little of the solution of zinc sulphate in water, (taken in a test tube) is added first a little and then excess of the ammonia solution. | At first a white ppt. is formed which disappears on further addition of ammonia solution. | The white ppt is due to zinc hydroxide :<br>$ZnSO + 2NH_4OH = Zn(OH)_2 + (NH_4)_2SO_4$.<br>In excess ammonia solution, zinc hydroxide dissolves due to the formation of a complex salt, which is soluble in water :<br>$Zn(OH)_2 + 6NH_4OH = Zn(NH_3)_6](OH)_2 + 6H_2O$. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| (iv) To a little of an aquesous solution of silver nitrate ($AgNO_3$) is added first a little, and then an excess of ammonia solution. | At first a brownish ppt. is formed, which dissolves in excess of ammonia solution. | At first, ppt. of silver hydroxide is obtained, which being unstable, immediately breaks up into silver oxide, having brownish appearance :<br>$AgNO_3 + NH_4OH = AgOH + NH_4NO_3$<br>$2AgOH = Ag_2O + H_2O$.<br>$Ag_2O$, thus formed, dissolves in excess of ammonium hydroxide, forming soluble silver ammine hydroxide :<br>$Ag_2O + 4NH_4OH = 2[Ag(NH_3)_2]OH + 3H_2O$. |
| (v) To a little of an aqueous solution of ferric chloride is added, at first, a little and then, an excess of ammonia solution. | A reddish brown ppt. is formed which does not dissolve in excess of ammonia solution. | The reddish brown ppt. is due to ferric hydroxide which is insoluble in excess of ammonia solution :<br>$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl$. |
| (vi) Similar experiments are performed with : | | |
| (a) an aqueous solution of aluminium sulphate. | A colourless gelatinous ppt. forms, which does not dissolve in excess of ammonia solution. | The gelatinous ppt. in due to aluminium hydroxide which is insoluble in excess of ammonia :<br>$Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3 + 3(NH_4)_2SO_4$. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| (b) an aqueous solution of magnesium sulphate. | A white ppt. is obtained, which does not dissolve in excess of ammonia solution. | The white ppt. of magnesium hydroxide does not dissolve in ammonia : $MgSO_4 + 2NH_4OH = Mg(OH)_2 + (NH_4)_2SO_4$. |
| (vii) To a little of the ammonia solution is added a few drops of Nessler's reagent.* | A reddish brown (or brownish yellow) colour or ppt. appears.<br>[N.B. With smaller quantity of ammonia, a colour is produced, while with sufficient amount of ammonia a ppt. is obtained.] | Ammonia reacts with the reagent, forming an unstable compound having a reddish brown (or brownish yellow) colour. |

---

* Nessler's reagent is an aqueous alkaline solution of $K_2HgI_4$.

It is prepared by adding KI solution to $HgCl_2$ solution till the red ppt. of $HgI_2$ first formed just re-dissolves in excess of KI solution. It is then made alkaline.

$$HgCl_2 + 2KI = 2KCl + HgI_2 \text{ (red ppt.)}$$
$$HgI_2 + 2KI = K_2[HgI_4].$$

**Precautions.**—(i) The hard-glass test tube should be clamped with its mouth slightly inclined downwards.*

(ii) The apparatus and the ingredients should be dry.

(iii) Heating of the mixture should be done at first slowly and then strongly.†

---

* & † for similar reasons as stated in the foot-notes in page 41.

## 5. SULPHURETTED HYDROGEN

### Hydrogen Sulphide ($H_2S$).

**Principle of preparation.**—In the laboratory, sulphuretted hydrogen is prepared by the action of dil. $H_2SO_4$ on ferrous sulphide (FeS): $FeS + H_2SO_4 = H_2S + FeSO_4$.

For demonstration of its preparation and experimentation on its properties, the gas is prepared in the laboratory in a Woulf's bottle. But, it is an important analytical reagent and is widely used for the separation and identification of various metallic ions in solution. For this purpose, it is required to have a ready and intermittent supply of the gas at hand in the laboratory. To meet this requirement, a Kipp's apparatus is used.

**(1) The method using Woulf's bottle.**

**Apparatus required:** A Woulf's bottle (500 ml.), single-bored corks (2), a thistle funnel, a delivery tube doubly bent at right angles, a few gas jars with lids.

**Chemicals required:** Some pieces of ferrous sulphide, dil. $H_2SO_4$, some tapers, blue litmus solution, caustic potash solution, dil. and conc. $HNO_3$, lead acetate solution, solutions of arsenious chloride, antimony chloride, stannous chloride, copper sulphate, zinc sulphate and magnesium sulphate.

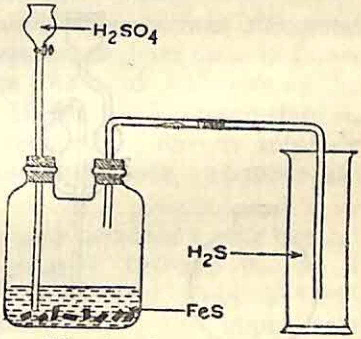


Fig. 4-5. Preparation of $H_2S$ in the laboratory.

**Procedure:** The procedure of this method, including the set up of apparatus, is exactly the same as that described for the preparation of carbon dioxide (p. 42), except that small pieces of ferrous sulphide and dilute sulphuric acid are usually used in this case as the ingredients. Sulphuretted hydrogen is heavier than air and so it is also collected in gas jars by upward displacement of air. To test whether a gas jar has been completely filled up with sulphuretted hydrogen or not, a filter paper soaked with lead acetate solution is held at the mouth of such a jar ; if the paper is turned black, the jar may be taken to be completely filled up with the gas.

(2) **The method using Kipp's apparatus.**

**Description of the apparatus.**—The apparatus consists of three glass globes set one above the other. The upper-most globe (1) is provided with a long stem tappering downwards. The first globe is fitted air-tight by ground-glass joint into the neck of the second (or the central) globe (2), while its stem reaches almost the bottom of the third (or the lower-most) globe. The mouth of the first globe is kept either open or closed by a rubber stopper through which a thistle funnel, provided with a long and bent narrow stem (3) is fitted, which acts both as a safety outlet of the acid when the pressure of the gas inside the apparatus suddenly rises, and also as an inlet for introducing acid.

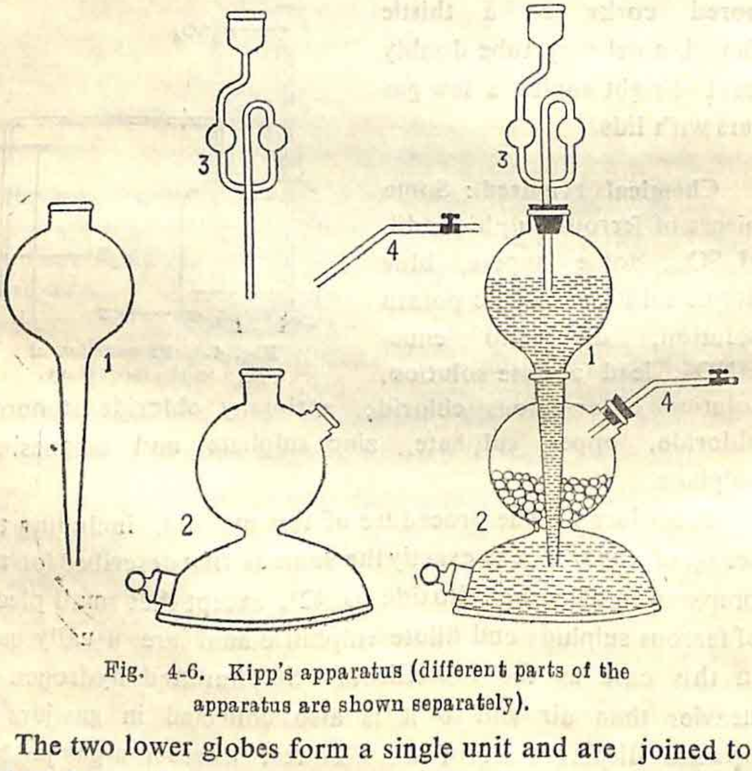


Fig. 4-6. Kipp's apparatus (different parts of the apparatus are shown separately).

The two lower globes form a single unit and are joined together by a short narrow neck. The lower-most globe is flattened at the bottom so that it may rest on the working bench, and it has an outlet closed by a stopper in order to drain off the waste liquid from time to time. The central globe is provided with an exit tube fitted with a stopcock for the escape of $H_2S$.

**Procedure.**—(*i*) Almost one-half of the central globe is filled up with small pieces of ferrous sulphide.

(*ii*) The stop-cock of the central globe is kept open and sufficient quantity of dilute sulphuric acid is poured down the thistle funnel until it fills the lower-most globe and comes in contact with ferrous sulphide in the central globe. More acid should then be added so that the pieces of ferrous suphide are covered with it. Ferrous sulphide, in contact with acid, evolves sulphuretted hydrogen, which passes out through the open stopcock. The stopcock is now closed. Under this condition, the gas produced within the central globe will not find any outlet and hence, it will be collected within this globe. Accumulation of considerable amount of gas within the globe causes development of sufficient pressure to drive the acid down into the lower-most globe, whence the acid will rise up the stem into the upper-most globe. Under such circumstances, the reaction ceases, since the two reactants [ ferrous sulphide and the acid ] are no more in contact and hence, no more gas evolves.

When the gas is needed, the stopcock attached to the central globe is opened and the gas escapes through it. As a consequence, the pressure inside the central globe falls and hence, the acid comes down by gravity from the upper-most globe and enters the central globe, where it reacts with ferrous sulphide, giving a fresh supply of the gas.

**Study of the properties of hydrogen sulphide.**

To study the properties of hydrogen sulphide, the following experiments are performed with the gas prepared and the observations with inferences are noted :

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. The gas is examined to observe its colour and to detect its odour. | No colour, but an obnoxious smell like that of rotten eggs is obtained. | Sulphuretted hydrogen is colourless, but possesses a disagreeable smell like that of rotten eggs. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 2. A lighted taper is introduced inside a jar of sulphuretted hydrogen | The taper is extinguished and the gas does not catch fire. | $H_2S$ is neither combustible nor a supporter or combustion : |
| 3. A lighted taper is held inside a gas jar full of air (placed upright) and then the jar of $H_2S$ is held inverted over the first at an inclined position, so as to pour down the gas. | The taper is extinguished immediately. | $H_2S$ is heavier than air, so that it can be transferred from one vessel to another by pouring. |
| 4. The gas is passed (bubbled) for some time through some quantity of water taken in a beaker, and to this water is then added a little blue litmus solution. | Blue litmus turns red. | The gas is slightly soluble in water and the water solution is acidic. |
| 5 A jar of $H_2S$ is held inverted into an aqueous solution of caustic potash. | The caustic potash solution gradually rises up in the gas jar and after some time, it fills the jar. | $H_2S$ is acidic in nature ; so, it dissolves and reacts with caustic potash soln. readily :<br>$KOH + H_2S = KHS + H_2O$. |
| 6. *Reactions with different metallic ions in solution* :<br>$H_2S$ is passed through the following solutions of different metallic ions : | | |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| (i) Mercuric chloride ($HgCl_2$) solution, acidified with dil. HCl. | A black ppt. is obtained. | $H_2S$ precipitates mercuric ion as mercuric sulphide (coloured black), which is insoluble in dil HCl.<br>$HgCl_2 + H_2S = HgS + 2HCl$.<br>(black). |
| The black ppt. is heated with dil. $HNO_3$. | The ppt. does not dissolve. | HgS is insoluble in dil. $HNO_3$. |
| (ii) Lead acetate [$Pb(CH_3COO)_2$] solution. | A black ppt. is obtained. | The black ppt. is due to lead sulphide (PbS):<br>$Pb(CH_3COO)_2 + H_2S = PbS + 2CH_3COOH$ |
| The black ppt. is treated with dil. $HNO_3$ (warm). | The ppt. dissolves. | PbS is soluble in warm dil. $HNO_3$. |
| (iii) Aqueous solution of copper sulphate ($CuSO_4$), containing dil. HCl. | A black ppt. is obtained. | The ppt. is due to copper sulphide:<br>$CuSO_4 + H_2S = CuS + H_2SO_4$. |
| The ppt. is treated with dil. $HNO_3$ (warm). | The ppt. dissolves. | CuS is soluble in dil. $HNO_3$, but insoluble in dil. HCl. |
| (iv) Aqueous solution of arsenious chloride ($AsCl_3$), containing dil. HCl. | A yellow ppt. is obtained. | The ppt. is of arsenious sulphide ($As_2S_3$), which is insoluble in dil. HCl as well as in conc HCl:<br>$2\,AsCl_3 + 3H_2S = As_2S_3 + 6HCl$. |
| The ppt. is treated with conc. HCl and warmed, | The ppt. does not dissolve. | |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| (v) Aqueous solution of antimony chloride ($SbCl_3$), containing dil. HCl. | An orange ppt. is formed. | The ppt. is due to antimony sulphide ($Sb_2S_3$), which is insoluble in dil. HCl, but soluble in warm conc. HCl :<br>$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$ |
| The ppt. is treated with conc. HCl and warmed. | The ppt. dissolves. | |
| (vi) Aqueous solution of stannous chloride ($SnCl_2$), containing dil HCl | A brown ppt. is obtained. | The ppt. is of stannous sulphide (SnS), which is insoluble in dil. HCl, but soluble in warm conc. HCl :<br>$SnCl_2 + H_2S = SnS + 2HCl$. |
| The ppt. is treated with conc HCl and warmed. | The ppt. dissolves. | |
| (vii) Aqueous solution of zinc sulphate $ZnSO_4$), containing dil. HCl. | No ppt. is formed. | — — |
| Aqueous solution of zinc sulphate, made alkaline with $NH_4OH$. | A white ppt. is formed. | The ppt. is due to zinc sulphide (ZnS), which is insoluble in alkaline ($NH_4OH$) medium, but soluble in dil. acid: $ZnSO_4 + H_2S = ZnS + H_2SO_4$. |
| The ppt. is treated with dil. HCl. | The ppt. dissolves. | |
| (viii) Aqueous solution of magnesium sulphate ($MgSO_4$), containing dil. HCl. | No ppt. is formed | In both the cases no ppt. is obtained, because magnesium sulphide is soluble in both dil. acid and $NH_4OH$. |
| Aqueous solution of magnesium sulphate, made alkaline with $NH_4OH$. | No ppt. is formed. | |

**Precautions.**—(i) The apparatus should be air-tight [and the stop-cock (Kipp's apparatus) should always be kept closed while not in use ; otherwise, any leakage of the gas would fill the laboratory with disagreeable smell. The gas is also poisonous.]

(ii) The outer end of the exit tube should reach almost the bottom of the jar.

(iii) FeS sticks should be hammered and broken into small pieces before use.

---

## 6. HYDROGEN CHLORIDE (HCl).

---

**Principle of preparation.**—Hydrogen chloride is prepared in the laboratory by heating a mixture of sodium chloride (common salt) and concentrated sulphuric acid :

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

[ N.B. This reaction occurs at moderate temperature (200°C). If, however, the temperature is raised to about 500°C further evolution of hydrogen chloride occurs according to the reaction :

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl ;$$

but, this is not actully done in practice owing to the danger of cracking the reaction-vessel and also due to the fact that $Na_2SO_4$ is much less soluble in water than $NaHSO_4$. At the end of the operation, it becomes difficult to remove the residue of $Na_2SO_4$ from the reaction-vessel, since on cooling, it forms a hard solid mass which is not easily soluble in water, nor it can be easily broken down and so, the reaction-vessel is often damaged. It is, therefore, advised to heat the reaction-mixture solwly with low Bunsen flame and not to raise the temperature too much, so that the second reaction can occur.]

**Apparatus.**—(i) A round-bottomed flask, (ii) A thistle funnel. (iii) A delivery tube, doubly bent at right angles, (iv) A few gas jars with lids, and cork, Bunsen burner, tripod stand, wire-gauze etc.

**Chemicals required.**—(i) Common salt (or sodium chloride) (ii) Conc. Sulphuric acid, (iii) Ammonium hydroxide, (iv) Silver nitrate solution etc.

**Procedure.**—(i) Some amount of common salt is taken in the round-bottomed flask which is placed upon a tripod stand over a wire-gauze and fixed to the stand by a clamp. To the mouth of the flask is fitted a cork having two bores, through one of which is introduced a thistle funnel, the lower end of its stem reaching almost the bottom of the flask, and through the other, the shorter arm of the delivery tube is so introduced that its lower end goes slightly below the cork. The outer end of the delivery tube (i.e. the longer arm) is kept inside a gas jar placed upright and covered by a lid as far as possible.

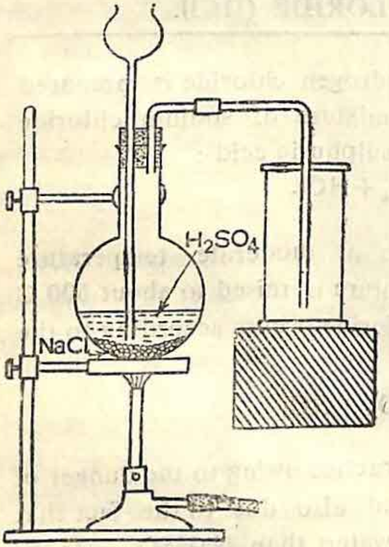


Fig. 4-7. Preparation of hydrogen chloride in the laboratory.

(ii) Some quantity of conc. $H_2SO_4$ is now introduced inside the flask through the thistle funnel, when reaction starts immediately and some hydrogen chloride is produced. When the signs of the initial reaction cease, the mixture is heated slowly by a Bunsen flame, when hydrogen chloride is produced in largar quantities and escapes through the delivery tube and collects in the gas-jar by upward displacement of air. (Hydrogen chloride is heavier than air.) To test whether the jar has been filled up by the gas or not, a glass rod, moistened with ammonia solution, is held at the mouth of the jar ; if dense white fumes are produced, then the jar is taken to be filled up completely. It is removed and kept on the table by covering it with a lid. In this way, a few more jars are filled up with hydrogen chloride and stored for further experiment.

**To prepare hydrochloric acid.**—Hydrochloric acid is a solution of hydrogen chloride in water. Hydrogen chloride is highly soluble in water and hence, it offers no difficulty in preparing its aqueous solution. And, in fact small quantities of dilute hydrochloric acid solutions, required for studying the properties in the laboratory (as stated below), can be readily prepared by pouring small quantity of water in a jar of hydrogen chloride, closing the mouth of the jar with a glass lid and shaking.

But, if relatively greater amount of hydrochloric acid is required to be prepared, the hydrogen chloride gas is to be directly led into water contained in a receiver, and in this case, care must be taken to avoid dangerous explosion by the back-suction of water to the hot reaction-mixture (containing hot conc. $H_2SO_4$) which is caused due to the rapid dissolution of hydrogen chloride in water. A modified safe method is described below.

**The method of dissolution of hydrogen chloride in water.**—The procedure for preparing hydrogen chloride is the same as described above. The outer end of the delivery tube is connected to an empty flask with the help of a cork. Another delivery tube, bent twice at right angles, is taken, and its one arm is introduced through the cork inside the empty flask and the other arm is placed well below the level of water taken in a beaker.

Hydrogen chloride gas, coming out through the delivery tube of the reaction-vessel, passes through the empty flask and then along the delivery tube fitted to it and comes in contact with water, where it is dissolved, forming a dil. aqueous solution of hydrochloric acid

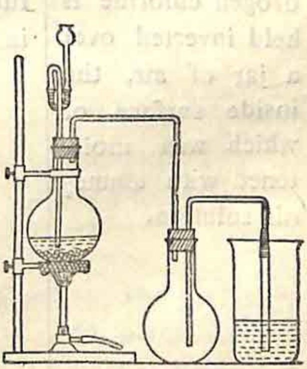


Fig. 4 8.—Preparation of hydrochloric acid.

Due to high solubility of hydrogen chloride in water, it may often create some vacuum inside the apparatus,due to which water would be sucked back from the beaker to the empty flask. If there were no empty flask in between, the water would have been sucked directly into the hot reaction-vessel, causing the flask to shatter violently.

**Study of the properties of Hydrogen chloride [and Hydrochloric Acid].** —To study the properties of the gas (hydrogen chloride) and/or of its aqueous solution (hydrochloric acid); the following experiments are performed and the observations with inferences are noted :

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. A jar of hydrogen chloride is examined to observe its colour and to detect its odour. | No colour, but a pungent smell is obtained | Hydrogen chloride is a colourless gas with a pungent smell. |
| 2. A lighted taper is introduced inside a jar full of hydrogen chloride. | The taper is extinguished and the gas does not catch fire. | Hydrogen chlorideis neither combustible nor a supporter of combustion. |
| 3. A jar of hydrogen chloride is held inverted over a jar of air, the inside surface of which was moistened with ammonia solution. | Dense white fumes are formed in the lower jar. | (i) Hydrogen chloride is heavier than air and hence, it comes down easily from the upper to the lower jar.<br>(ii) Hydrogen chloride reacts with ammonia, producing ammonium chloride ($NH_4Cl$), which appears in the form of dense white fumes : $NH_3 + HCl - NH_4Cl$. |

| *Experiments* | *Observations.* | *Inferences* |
|---|---|---|
| **4. Fountain experiment.** A small round-bottomed flask(250 ml. capacity) is filled up with hydrogen chloride and fitted with a bored cork at the mouth ; through the bore is introduced a glass tube with a jet at the upper end. The flask is now held inverted over blue litmus solution in water. | Blue litmus solution rushes into the flask in the form of a fountain and it turns red. | (i Hydrogen chloride is highly soluble in water.<br>(ii) The water solution of hydrogen chloride is acidic (hydrochloric acid), which turns blue litmus solution red. |
| 5. The *solution of hydrogen chloride in water* (i.e. hydrochloric acid) may be prepared as described in in page 61 or as in expt. 4 (above). With hydrochloric acid, the following experiments are performed : | | |
| (i) A little of $AgNO_3$ solution is taken in a test tube, and to it is added a little of the hydrochloric acid. | A curdy white ppt. is formed | The ppt. is due to silver chloride (AgCl) which is insoluble in water :<br>$AgNO_3 + HCl$<br>$= AgCl \downarrow + HNO_3$. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| The ppt. is divided into two parts To one part is added dil. $HNO_3$. | The ppt. does not dissolve. | Silver chloride is insoluble in dil. $HNO_3$. |
| And the other part is shaken with $NH_4OH$ solution. | The ppt. is completely dissolved. | Silver chloride is soluble in $NH_4OH$ solution due to the formation of a complex compound $[Ag(NH_3)_2]Cl$ :<br>$AgCl + 2NH_4OH = [Ag(NH_3)_2]Cl + 2H_2O$. |

**Precautions.**—(i) The apparatus should be air-tight. (ii) Heating should be done slowly and temperature must not be allowed to rise above 200°—250°C. (iii) Care must be taken so that water is not sucked back into the hot reaction-mixture during the preparation of aqueous solution of HCl gas (hydrochloric acid).

## ORAL QUESTIONS

1. Is hydrogen combustible ? Is it explosive ?

2. Which one reduces potassium permanganate solution—ordinary molecular hydrogen or nascent hydrogen ?

3. Is oxygen combustible ? Does it form an explosive mixture with any other gas known to you ?

4. What is a catalyst ? Mention the use of a catalyst known to you ?

5. Is ammonia acidic, neutral or basic ?

6. When an aqueous solution of ammonia is added in excess to an aqueous solution of copper sulphate, a deep blue solution is obtained. Why ?

7, Carbon dioxide is not poisonous, but no animal can live in it. Why ?

8. Carbon dioxide does not support combustion, but a lighted ribbon of magnesium burns in it brilliantly. Why ?

9. A gas has the odour like that of rotten eggs. Guess the gas.

10. Sulphuretted hydrogen is passed through an aqueous solution of lead acetate. What would happen ?

11. Hydrogen chloride gas is passed through water taken in a beaker. What would happen ?

12. Hydrogen chloride gas is passed through an aqueous solution of silver nitrate. What would happen ?

13. How can you show that carbon dioxide is an acidic oxide ?

14. How would you prove that ammonia is highly soluble in water ?

15. How can you prove that an aqueous solution of ammonia is alkaline ?

16. State the changes of colour of methyl orange indicator, when added to aqueous solutions of (i) carbon dioxide, (ii) hydrogen chloride, (iii) ammonia and (iv) hydrogen sulphide.

## 5

## STUDY OF THE CHEMICAL BALANCE AND WEIGHING OF SUBSTANCES

A balance is one of the most important tools in a chemical laboratory, since it is indispensible for quantitative analytical work. It is, therefore, essential to have a proper knowledge and understanding of its construction, use and care. The construction of, and the principle of weighing in a chemical balance will be discussed in this section.

**The Balance and the Measurement of Mass.**—The *mass* of a body can be determined by weighing in a balance. Every one of us must have seen a grocer's balance and the procedure in weighing a substance. It consists of a straight uniform rod, called the *beam*, from the two ends of which two identical *pans* are suspended. The beam is pivoted at its middle point, so that with empty pans, the beam remains perfectly horizontal when freely suspended. The substance to be weighed is placed on the right pan and standard weights are placed by trial on the left pan, till the beam becomes horizontal again. Under such conditions, the weight of the substance is equal to the *weights* placed on the left pan. Such balances are, however, suitable for gross weighing, and they are not sensitive enough to weigh very light objects. For the purpose of chemical analysis, much more sensitive and accurate balances are necessary, which can work with high precision.

**Description of a common chemical balance** : The essential *parts* of a common chemical balance are (Fig 5-1) :

(1) The **Balance beam.**—It is a horizontal metal or alloy casting, generally of the form of a thin bar, which is capable of turning freely about a sharp steel or agate *knife-edge* at the middle, which is called the *fulcrum*. The sharp end of the knife-edge rests on a small plate of steel or agate to minimise friction. At the ends of the beam, two similar agate knife-edges are attached with their sharp edges upwards.

(2) The **Stirrups** or **Pan supporters.**—These rest on the terminal knife-edges. In the better type of balances, these are provided with agate pieces attached at the lower surfaces of their upper arms. These are furnished with hooks at the lower end, from which the pans are suspended. The distances from the fulcrum to the centre of gravity of the stirrups are called the *arms* of the balance, which are equal in length.

(3) The **Scale pans**, on which standard *weights* and substance to be weighed are placed.

(4) The **Pillar**, attached to the base-plate of the instrument to support the beam when at rest, is a vertical rod encased within an outer cover, and it can be raised or lowered by a key or knob at the base, when required The pillar has an agate at the top, upon which the central knife-edge of the beam rests.

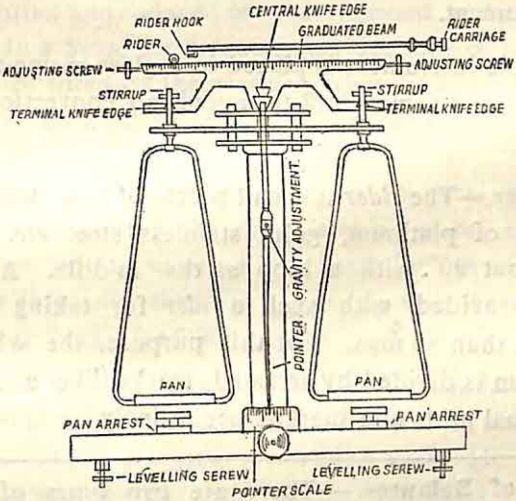


Fig. 5-1.—Different parts of a chemical balance.

(5) The **Pointer.**—This is attached at its upper end to the middle part of the beam and the lower end can move freely over a graduated scale attached to the bottom of the pillar. When the beam is horizontal, the pointer should be vertical and its lower end should point to the zero mark of the scale.

(6) The **Arresting arrangement.**—When the balance is not in use, the pillar supporting the beam is lowered, so that

the beam rests on another support attached to the outer casing of the pillar as horizontal projections, and the under-surfaces of the pans just touch the pan-arrests on the base-board. Thus, the knife edge at the centre of the beam does not always rest on the agate plate and so its sharpness is preserved.

(7) **The Adjusting nuts.**—At each end of the beam, there is a nut working in a screw. By displacing the position of the nuts, the effective weight on each side can be altered through a small range, and thus weighing accuracy of the balance can be adjusted.

(8) **The Plumb line** and **the Levelling screws.**—The base of the instrument is provided with levelling screws, by whose adjustment the pillar is made vertical, so that the balance-beam becomes horizontal ; the correct adjustment is indicated by the exactly vertical position of the plumb line attached to the instrument.

The whole instrument is placed in a glass-casing to protect it from dust (and fumes) and to avoid air convection during weighing.

**The Rider.**—The *rider* is small piece of wire weighing 10 mgs., made of platinum, gold, stainless steel *etc.* and bent twice at about 90°. with a loop at the middle. A chemical balance is provided with such a *rider* for taking fractional weights less than 10 mgs. For this purpose, the whole of the balance beam is divided by serrated marks (like a saw blade) into 100 equal parts and marked accordingly.

---

**Types of Balances.**—There are two types of balances generally used in the chemical laboratories—*Sartorius* type and *Bunge* type. In the *Sartorius type* of balances, the markings on the balance beam start from '*zero*' at the centre of the beam, with 10 equal divisions on both sides, (marked 1 to 10), each division being sub-divided into 5 equal parts. In the *Bunge type* of balances, the '*zero*' mark is at the extreme left of the beam, whose length is divided into 10 equal divisions (1 to 10), each division being sub-divided into 10 equal parts.

**The use of rider during weighing in a chemical balance.**—While weighing, if it is found that weights less than 10 mgs. (which are not provided with in the weight box) are required for correct balancing, the *rider* is moved by the *rider carriage* and placed by *trial and error method* on a suitable position on the beam. From the position of the rider on the scale engraved on the beam, the extra weight is calculated and added to the '*weights*' placed on the pan. Each smaller subdivision on the beam of the *Sartorius* balance corresponds to 0·2 mgs. and in the *Bunge type*, it is 0·1 mg. *Sartorius* type of balances are commonly used in chemical laboratories.

---

N. B. The *Bunge* type balances are almost similar to the *Sartorius* type. The only point the students should remember that, while weighing in a Bunge balance, the rider should be placed on the *zero* mark, even though it is not in use. It should be lifted and placed in the relevant position when required. In a *Sartorius* balance, the rider may be kept on the 'zero' mark or lifted on the carriage, when it is not in use. It should be placed on the relevant position whenever required.

---

**Calculation of extra weight due to the use of rider.**—In a *Sartorius* balance, if the *rider* is to be placed on the 3rd larger divison of the scale on the beam for exact counterpoising of a substance, then the additional weight from the use of the rider is 3 mgs. (=0·003 gms.).

If the *rider* is to be placed on the second smallest division after the 3rd larger divison on the scale for this purpose, the additional weight is 3·4 mgs. (=0·0034 gms.). [It is always advisable *not* to place the rider on the left-hand side of the 'zero' mark. If such case arises, lower the *weights* placed on the pan of the balance and then counterpoise.] It is thus seen that the exact value of the weight of a substance upto the third or even fourth places of decimals can be obtained from an ordinary chemical balance by the use of *rider*.

**The Weight Box :** It is a wooden box with hinged lid. The standard *weights* are kept in the grooves cut in the box. The standard *weights* are generally made of brass, plated with nickel or chromium (stainless steel *weights* are also available). A standard set generally comprises the following *weights* :

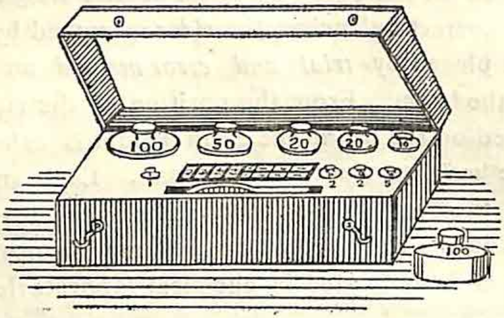


Fig. 5-2.—A weight box used with a chemical balance.

| | | | |
|---|---|---|---|
| 100 gms. | 1 no. | 500 mgs. | 1 no. |
| 50 gms. | 1 no. | 200 mgs. | 2 nos. |
| 20 gms. | 2 nos. | 100 mgs. | 1 no. |
| 10 gms. | 1 no. | 50 mgs. | 1 no. |
| 5 gms. | 1 no. | 20 mgs. | 2 nos. |
| 2 gms. | 2 nos. | 10 mgs. | 1 no. |
| 1 gm. | 1 no. | | |

The heavier weights (upto 1 gm.) are more or less cylindrical solid metal blocks with a knob at the top, while the fractional weights are generally rectangular or triangular metal plates. The value of each *weight* is inscribed or embossed on it. The *weights* are arranged in the box in a regular way and the *fractional weights* are generally covered by a glass plate. A pair of forceps is also provided in the box for handling the weights.

**The Use of a chemical balance**: *Points to be followed before, during and after the weighing in a chemical balance :—*

(1) The balance should be kept on a strong table so that it is not affected by vibration It should be placed in a room free from dust and fumes

(2) The balance may not be found correct at all times whenever it is opened for use. The main defects may be the following :

(i) The balance may not be properly levelled. This is easily detected by looking at the *plumb-line*, which should not be exactly vertical under such conditions. This defect should be corrected by adjusting the *levelling screws* provided at the base of the instrument, till the *plumb line* is *exactly vertical.*

(ii) The beam of the balance may not be perfectly horizontal when freed, *i.e.* one side is heavier than the other side.

This is easily detected by unequal oscillations of the pointer on each side of the zero mark of the scale. This can be adjusted by screwing in or out the nuts provided at the ends of the beam of the balance. The correct adjustment is obtained when the pointer practically rests at the middle of the scale or oscillates equally on both sides of the zero mark on the scale.

(iii) The stirrups may be displaced. If the stirrups are displaced from their proper positions due to prior rough handling, correct weighing cannot be done. The stirrups should be properly placed on the beam before weighings are made.

(3) The pans may not be clean. The pans should be properly cleaned by a camel-hair brush before using the balance.

(4) A hot body must not be weighed in a chemical balance.

(5) The doors of the balance box should be kept closed when the weighing is done (i.e. when oscillations of the pointer are observed). The doors should be opened only when putting in or taking out the weights or the substance to be weighed. The doors should be kept well-closed after the weighing is over.

(6) The balance beam and the pans should the *arrested* by lowering with the key before adding or removing the *weights* or the substance to be weighed.

(7) The *weights* should not be lifted with fingers. They should be handled with the forceps provided in the weight box. The *weights* should be kept in their proper places in the box after use.

(8) The swinging of the pointer should not be stopped abruptly by a *jerk*. The key should be operated for stopping the oscillations of the pointer only when it is near the *zero* mark of the scale.

N.B. *A chemical balance is a costly instrument and special care should be taken to see that it is not spoilt by rough handling.*

**The method of Weighing.**—To weigh a substance in a chemical balance, it is to be seen first that the balance is properly adjusted. For this purpose, the balance beam is raised by turning the *key* at the base slowly so that the beam swings freely. If the pointer oscillates equally on both sides of the zero mark of the scale, then the *key* is turned again in the other directon to arrest the oscillations of the beam. If unequal oscillations are observed, the instrument is to be adjusted as described earlier. Now, the side-doors of the balance-case are opened (it is advisable not to open the front door during weighing), and the substance to be weighed is placed on the left pan. [Chemicals should not be directly placed on the pan ; they should be kept on a watch glass or a weighing bottle (fig. 5-3) for weighing. ] Standard weights are now picked up from the weight-box with the help of the forceps and placed on the right pan. The actual selection of the *weights* to be placed is, however, to be made by *trial and error* method. A specific example will illustrate the actual procedure.

Fig. 5-3.— Weighing bottle.

**Example.**—Let the substance to be weighed is approximately judged to weigh between 20 – 30 gms. Then the respective *weights* are taken out from the weight-box (one 20 gms. and one 10 gms.-*weights*) with the help of the forceps and are placed gently on the right pan. Now, the *key* is turned slowly about half-way (the key should not be given a complete turn to release the beam fully) and the movement of the pointer is noticed. If it moves towards left, the *weights* placed on the right pan are heavier than the substance. So, the 10 gms.-*weight* is removed from the pan with the forceps and kept in its proper place in the weight-box. Then a 5 gms -*weight* is taken from the box and is placed on the pan. Again the beam is raised slightly by turning the *key* slowly about half way. This time, the pointer may move towards right, showing that the substance to be weighed is heavier than the *weights* placed on the pan. The beam is then lowered and a 2 gms.-*weight* is placed on the right pan and the movements of the pointer are observed as before. In this way,smaller *weights* are placed (upto

10 mgs.) on the right pan and the movements of the pointer noticed without fully releasing the beam (*i.e.* by turning the *key* half way only). Whenever the pointer moves towards the left with the addition of a particular *weight*, it should be understood that the *weights* are heavier than the weight of the substance, and hence, the added weight should be *replaced* by a smaller *weight*. It will generally so happen that the substance to be weighed cannot be exactly counterpoised by placing the weights (even by using the lowest 10 mgs.-weight available in the weight box, and the substance is slightly heavier. In these circumstances, the rider is to be used. To do this, the doors of the blance-case are closed and the rider is put (with the help of the rider-carriage) on a larger division-mark on the beam. Suppose it is placed on the first larger division on the right-hand side of the beam. The *key* is again half-turned to observe the movement of the pointer. If the pointer moves towards right, the substance is still heavier than the weights placed, and the rider is then to be shifted towards further right after lowering the beam. In this way, it may be observed that the pointer moves towards the left on placing the rider on a particular larger division-mark, and towards the right on placing the rider on the earlier mark. For example, it may swing towards the left on placing the rider on the third larger mark and towards the right on placing it on the second larger mark. In such cases, the rider is to be placed on the smaller division-marks in between the second and the third larger divisions. By trial, it may be found that, on placing the rider on the 3rd smaller division after the second larger mark, the pointer does not appreciably deflect on either side of the zero mark of the scale. The *key* is now fully turned (slowly and not with a jerk) to allow the beam to swing freely. It will be found that the pointer will oscillate equally on either side of the scale. The beam is then arrested completely by turning the *key*. The weight of the substance is equal to the combined *weights* placed on the right pan, together with that contributed by the rider. The *weights* are now taken out *one by one*, after noting its value on the note-book and placed inside the *weight-box* in their proper rooms. The reading of the rider is noted

and it is then placed on the zero-mark on the beam. As an illustrative example, the weight of the substance is recorded as follows:

The observed weight of the substance:
= [20 gms. + 5 gms. + 2 gms. + 1 gm.]
+ [500 mgs. + 200 mgs. + 50 mgs. + 20 mgs. + 10 mgs]
+ the weight due to the rider (23 smallest divs.)
= 28 gms. + 780 mgs. + 23 × 0·2 mgs* (rider reading)
= 28·7846 gms.

[* $\because$ each smallest division on the beam of a Sartorius balance $= \frac{10 \text{ mgs.}}{50} = 0{\cdot}2$ mgs.]

**To weigh a required amount of a substance.**—Although it is a comparatively easy task to weigh a given substance *as a whole* by choosing the correct weights by the *trial and error method* just now depicted, it is acually a difficult job to weigh out a required amount of the substance from its larger bulk. For example, if we are to weigh 2·54 gms. of a substance, we should first counterpoise a small watch glass in the balance, by placing it on the left pan and then place the *weights* (say, 2 gms. + 500 mgs. + 20 mgs. + 20 mgs.) on the right pan with the rider on the proper position. The substance to be weighed is then decanted slowly (by small bits) on the watch glass placed on the left pan (taking utmost care to see that not a speck of the substance falls outside the watch glass). The *key* is operated after each small addition to see that the amount of the substance transferred does not exceed the amount proposed to be taken out.

This is not, however, a satisfactory method; since, apart from the considerable loss of time entailed in such operations, it necessitates frequent *taking off* or *adding on* the substance from or to the watch glass on the pan. The *recommended procedure* of weighing out in such cases is to take the substance (a little more than what is to be weighed) in a *weighing bottle* (fig. 5 3). The correct weight of the weighing bottle (with its content) is taken as stated earlier. The weight is noted down

A little of the substance is then transferred carefully in a clean beaker or a measuring flask fitted with a small funnel, as the case may necessitate, and the weighing bottle is again weighed. If too little of the substance has been transferred (as shown by the loss in weight of the weighing bottle), a little more substance in again similarly transferred, till almost the required amount (a little less or more) of the substance has been transferred.

The weight of the substance taken is obtained from the difference of the two weights. This procedure is known as the *weighing by method of difference.* The following experiment is an illustrative example to demonstrate this method :

**Expt.**—Weighing a given quantity of a substance with the help of a chemical balance.

[Let about 1·527 gms. of a substance are to be weighed.]

Procedure : (i) The substance is taken in excess (*i.e.* a little more than the required amount) in a weighing bottle.

(ii) The weighing bottle containing the substance is placed on the left pan.

(iii) Weights are placed by trial on the right pan and the correct weight is taken (if necessary, by using the *rider*).

(iv) The balance is now set on arrests and the weight of the bottle plus the substance contained in it is noted.

(v) The bottle is then removed from the pan and approximately the required quantity of the substance (this depends on experience) is transferred to a beaker (or any other suitable vessel) carefully so that not a single speck of the substance drops outside.

(vi) The bottle is fitted with its stopper, placed on the pan and weighed again. The process may be repeated to transfer *almost* the required amount of the substance.

**Results** : The weight of the substance transferred to the beaker is tabulated and calculated as follows (a specific example is given) :

| *No. of weighing* | *Weight of the bottle + Substance* | | | | Weight of the substance taken ($W_1 - W_2$) |
|---|---|---|---|---|---|
| | Weights on the right pan | Rider reading | Value of rider reading | Total weight | |
| *First weighing* | 20 gms + 10 gms.<br>+ 1gm. + 100mgs<br>+ 20 mgs.<br>+ 20 mgs.<br>= 31 gms. + 140 mgs.<br>= 31·1400 gms. | 47 small divisions | 47 × ·0002<br>= 0·0094 gms. | 31·1400<br>+ ·0094<br>31·1494 gms<br>($W_1$) | 31·1494 gms.<br>29·6236 gms.<br>1·5258 gms. |
| *Second weighing* | 20 gms. + 5 gms<br>+ 2 gms. + 2gms.<br>+ 500 mgs<br>+ 100 mgs.<br>+ 20 mgs.<br>= 29 gms.<br>+ 620 mgs.<br>= 29·6200 gms. | 18 small divisions | 18 × ·0002<br>= 0·0036 gms. | 29·6200<br>+ 0·0036<br>29·6236 gms<br>($W_2$) | |

N.B. It may be noted that, although it was intended to weigh out 1·527 gms. of the substance, the weight of the substance actually taken is found to be 1·5258 gms. Though there is a difference between the two weights, no further attempt need be made for finer results, since it is *practically* very difficult to weigh exactly the amount required. In all analytical work the correct weight of the substance actually taken is noted and further calculations are done on this basis.

## ORAL QUESTIONS

1. What is the diffierence between an ordinary balance and a chemical balance ?

2. On which pan the standard weights are placed ?

3. Why should the balance beam be kept on arrests each time when removing or adding weights to the pan ?

4. 'Only the mass of a body, and not itweiht,ism net sured in a common balance'. —Discuss the statement.

5. Is it justified to weigh a hot body in chemical balance ? If not, why ?

6. Why is it advised to keep the doors of the balance-case closed during swinging of the pointer ?

7. Why is a body weighed by the method of oscillations ?

8. Why is it very difficult to weigh out exactly the amount of the substance required ?

9. What is the method of *weighing by difference* ?

10. What is a rider ? Why is it used, and how ?

# 6

# DETERMINATION OF EQUIVALENT WEIGHTS OF METALS

**Equivalent Weight.**—The equivalent weight of an element is defined as the parts by weight of the element, which combine with or displace from a compound 8 parts by weight of oxygen or 1·008 parts by weight of hydrogen or 35·46 parts by weight of chlorine.

Thus, if $W_x$ gms. of an element (X) combine with $W_O$ gms. of oxygen or $W_H$ gms. of hydrogen or $W_{cl}$ gms. of chlorine(or displace from their compounds the above parts by weight of these elements respectively), then according to the definition, the equivalent weight of the element,

$$E_x = \frac{W_x}{W_O} \times 8, \text{ or, } \frac{W_x}{W_H} \times 1{\cdot}008, \text{ or, } \frac{W_x}{W_{cl}} \times 35{\cdot}46.$$

**Example** (*1*). *Metallic copper, when burnt in air (oxygen), yields black copper oxide. It has been found that 63·5 gms. of copper give 79·5 gms. of cupric oxide :*

$$2Cu + O_2 = 2CuO$$

$$\begin{array}{lll} 2 \times 63{\cdot}5 & 2 \times 16 & 2 \times [63{\cdot}5 + 16] \\ \text{or } 63{\cdot}5 & 16 & 79{\cdot}5 \end{array}$$

Thus, according to the reaction,

63·5 gms. Cu combine with $79{\cdot}5 - 63{\cdot}5 = 16$ gms. of oxygen

So, 8 parts by weight of oxygen combine with

$$\frac{63{\cdot}5}{16} \times 8 = \frac{63{\cdot}5}{2} = 31{\cdot}75 \text{ parts by weight of copper.}$$

∴ the equivalent weight of copper = 31·75.

(2) *Metallic magnesium, when reacted with dil. hydrochloric acid, produces magnesium chloride by displacing hydrogen from the acid :*

$$\begin{array}{ccccccc} Mg & + & 2HCl & = & MgCl_2 & + & H_2 \\ 24 & & & & 95 & & 2 \end{array}$$

It is found that 24 gms. of metallic magnesium displace 2 gms. of hydrogen from hydrochloric acid. Therefore, the equivalent weight of magnesium $=\frac{24}{2}\times 1=12$.

[The weight of a molecule of hydrogen is actually $=2\times 1{\cdot}008 = 2{\cdot}016$, but for simplicity of calculations, it has been taken to be 2 and so, the atomic weight of hydrogen $=1$.]

N. B. Equivalent weight is a pure *number*, it has no unit.

If the atomic weight of an element and its valency in one of its compounds are known, its equivalent weight in that compound can be calculated by using the equation,

**Atomic weight = Equivalent weight × valency.**

Thus, the atomic weight of magnesium is 24 and its valency in $MgCl_2$ is 2.

So, Equivalent weight of Mg $=\frac{24}{2}=12$.

There are several other methods for the determination of equivalent weight of an element. These are :

(i) By conversion of the element into its oxide
(ii) By " " " " its chloride.
(iii) By reduction of an oxide of the metal.
(iv) By displacement of hydrogen from an acid by the metal.

[ For details of these methods, see "Poddar & Haldar, Higher Secondary Chemistry." §7. ]

**Expt. Determination of the Equivalent Weight of Magnesium : Hydrogen displacement method.**

**Principle of determination.**—This method of determination of equivalent weight is based on the relationship, Equivalent weight of a metal

$$=\frac{\text{Weight of the metal (W)}\times 1{\cdot}008.}{\text{Weight of hydrogen displaced by the weight(W)of the metal.}}$$

The method, thus, involves the determination of the weight of hydrogen that would be displaced by a known weight of the metal. To do this, a weighed amount (W gms.) of a pure metal (Magnesium) is allowed to react with dil. acid (*e.g.* dil. HCl or $H_2SO_4$), and the gas (hydrogen) evolved is collected. Its volume (V ml.) is measured at the temperature (t°C) and pressure (P mm.) of the laboratory. This volume is reduced to the volume at N. T. P., the weight of hydrogen in grams is calculated from its density and hence, the equivalent weight of magnesium is calculated as follows :

Let the volume of hydrogen at N.T.P. = V′ ml.

$$\therefore \quad \frac{760 \times V'}{273} = \frac{(P - f) \times V}{(273 + t)}, \text{ when } f = \text{aqueous tension at } t^\circ C.$$

$$\text{or,} \quad V' = \frac{(P - f) \times V \times 273}{760 \times (273 + t)}.$$

Now, 1 ml. of hydrogen weighs at N.T.P. 0·00009 gms.

∴ Weight of hydrogen displaced by W gms. of magnesium

$$= V' \times 0{\cdot}00009 \text{ gms.} = \frac{(P - f) \times V \times 273 \times 0{\cdot}00009}{760 \times (273 + t)} \text{gms.}$$

Hence, the equivalent weight of magnesium

$$= \frac{W \times 760 \times (273 + t)}{(P - f) \times V \times 273 \times 0{\cdot}00009} \times 1{\cdot}008.$$

From the experiment, the values of the terms P, V and t are known and the value of 'f' at the temperature of the laboratory (t°C) is noted from the table (see Table 1 given in the Appendix. Thus, equivalent weight of magnesium can be easily calculated with the help of this equation.

**Apparatus required.**—(i) A beaker (500 ml.). (ii) A small watch glass. (iii) A small glass funnel. (iv) A graduated glass tube closed at one end. (v) A tall cylindrical glass jar containing water. (vi) A thermometer. (vii) A barometer. (viii) A chemical balance.

**Chemicals required.**—(i) Pure magnesium metal. (ii) Dilute sulphuric acid.

**Procedure.**—(i) A weighed sample ($\sim$0·2 gms.) of pure magnesium is taken in a small watch glass which is placed within the beaker and covered by a funnel with its stem projected upwards. The beaker is then filled with sufficient distilled water so that the funnel with its stem remains under water.

(ii) The graduated tube is filled completely with water, leaving no air bubbles inside it, and is placed upside down over the stem of the funnel [Fig. 6-1 (a)].

(iii) Conc. $H_2SO_4$ is gradually added to water, a small quantity at a time. Reaction between acid and the metal, $Mg + H_2SO_4 = MgSO_4 + H_2$, starts within a short time and hydrogen begins to evolve and collect in the glass tube by displacement of water.

(iv) When the whole of the magnesium will be exhausted, the reaction will cease.

(v) Now, the glass tube is held with the help of a strip of paper and is taken out of the beaker, closing the open mouth by a thumb, and is placed in the tall jar full of water.

(vi) The tube is moved up and down to adjust the water inside and outside the tube at the same level [Fig. 6-1 (b)].

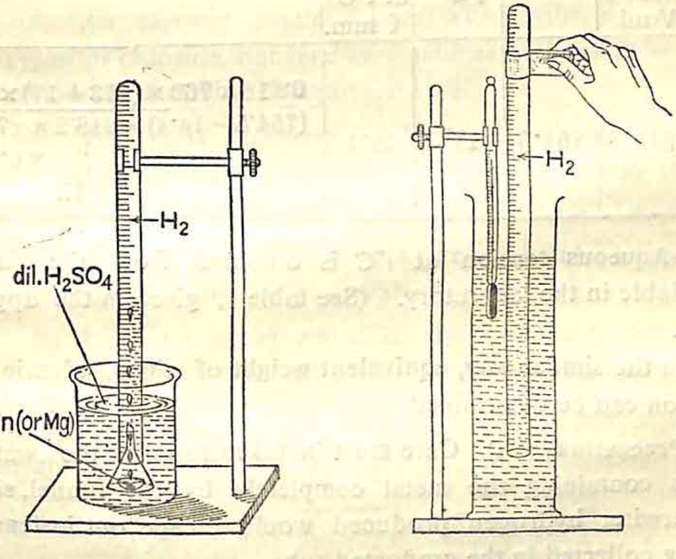


Fig. 6-1.—Determination of equivalent weight by hydrogen diplacement method: (a) Collection of hydrogen, (b) measurement of its volume.

(vii) The volume of the gas is now noted from the graduations on the tube.

(viii) The temperature of water, and the atmospheric pressure are noted with the thermometer and from the barometer respectively.

Barometer is usually kept in the laboratory at a definite place away from the place of experiment.

As a weighed sample is to be supplied to the students, they need not weigh themselves.

**Results and calculations :** The data (values of pressure, temperature, volume of the gas, weight of the metal *etc.*) as collected above are computed as shown in the table below, and the equivalent weight is calculated in the way as illustrated by a specific example :

| Weight of metal taken, W gms | Volume of hydrogen collected, V ml. | Pressure noted, P mm | Temperature noted, t°C | Aqueous tension* at t°C f mm. | Equivalent weight of the metal $= \frac{W \times 760 \times (273+t) \times 1{\cdot}008}{(P-f) \times V \times 273 \times 0{\cdot}00009}$ |
|---|---|---|---|---|---|
| 0·218 | 218·2 | 754·5 | 17° | 14·4 | $\frac{0{\cdot}218 \times 760 \times (273+17) \times 1{\cdot}008}{(754{\cdot}5 - 14{\cdot}4) \times 218{\cdot}2 \times 273 \times 0{\cdot}00009}$ <br> $= \mathbf{12{\cdot}12}$ |

*Aqueous tension at *t°C* is obtained from the *Table*, available in the laboratory. (See table 1, given in the appendix).

In the similar way, equivalent weight of zinc*, aluminium or iron can be determined.

**Precautions :** (i) Care must be taken to cover the watch-glass containing the metal completely by the funnel, since otherwise, hydrogen produced would escape out instead of being collected in the graduated tube.

(ii) The graduated tube containing hydrogen should not be held by hand, since the gas would then expand by the warmth of the hand and its correct volume cannot be obtained.

(iii) Levelling of water inside and outside the tube should be done carefully and correctly.

---

*When zinc is taken, a few drops of aqueous copper sulphate solution are to be added to start the reaction, since pure zinc does not react immediately with acid.

## ORAL QUESTIONS

1. What is meant by the equivalent weight of an element ? In what unit it is expressed ?

2. What is the relationship between equivalent weight and atomic weight of an element ?

3. If the valency and the atomic weight of an element are known, is it possible to know its equivalent weight ? If so, how ?

4. By what different methods can the equivalent weight of an element be determined ?

5. Suggest a method to determine the equivalent weight of carbon or silver.

6. An element reacts neither with hydrogen nor with oxygen or chlorine, but readily combines with sulphur. Is it possible to determine its equivalent weight ?

7. Why it is necessary to know the value of aqueous tension to calculate the equivalent weight of a metal through hydrogen displacement method ?

8. Can the equivalent weight of an element be the same as its atomic weight ? If so, when ?

9. How would you calculate the equivalent weights of (a) a compound, (b) an acid, (c) a base and (d) a salt ?

10. Can an element have more than one equivalent weights ? If so, when ?

7

# VOLUMETRIC ANALYSIS.

## ACIDIMETRY AND ALKALIMETRY.

**Volumetric Analysis :** In volumetric analysis, the quantity of a substance present in a definite amount of a given sample is determined, not by direct weighing, but *indirectly* by titrating a known volume of a solution of the sample with a standard solution of a suitable reagent, using an indicator, if necessary, to mark the end of the operation.

It is often advantageous and convenient to measure the volumes of solutions than to weigh a substance, and that is why the volumetric methods of analysis are, in general, more popular and largely practised. To measure the volumes of solutions accurately, some standard (calibrated) apparatus like *burette*, *pipette*, *measuring* (also called *volumetric*) *flask ete*. are used.

**Acidimetry and Alkalimetry.**—The method, with the help of which the strength of an acid is determind by titrating with a standard solution (*i.e.* of known strength) of an alkali, is called **Acidimetry**.

The method, with the help of which the strength of an alkali solution is determined by titrating with a solution of an acid of known strength, is called **Alkalimetry**.

N. B. According to some authors, the definitions of acidimetry and alkalimetry are just the reverse of what are given above.

**Terms and Expressions :**

(1) **Titration :** It is the operation through which the volume of one solution (containing a given substance) required to react completely with a known volume of a second solution (containing another substance) is found out, for the purpose of knowing the strength or concentration of one solution when that of the other is given.

In practice, one solution is taken in a burette and a measured volume of the other is taken in a conical flask(or beaker) by means of a pipette. The solution from the burette is allowed to flow slowly (with stirring) into the solution taken in the conical flask (or beaker). This is continued until the end-point of titration is reached, which is marked by a change in colour of the indicator used for the purpose.

(2) **Titrant and Titrate :** The solution which is used for the titration of other solutions is known as the titrant and the solution which is titrated with the help of the titrant is known as the titrate. Conventionally, the *titrant* is taken in the burette and the *titrate* is measured out by a pipette into a conical flask or beaker, which is placed beneath the burette during titration.

(3) **Indicator :** Indicators are chemical substances used during titrations in volumetric analysis to mark the end-point of titrations by change of their colours.

Some of the indicators which are often used in acid-base titrations are given below, along with their colours shown in acidic as well as in alkaline media.

| *Indicators* | *Colours of the indicators in* | | |
|---|---|---|---|
| | *neutral medium* | *acidic medium* | *alkaline medium* |
| 1. LITMUS SOLUTION | **Purple or Violet** | **Red** | **Blue** |
| 2. PHENOLPHTHALEIN | **Colourless** | **Colourless** | **Pink** |
| 3. METHYL ORANGE | **Orange** | **Pink or Red** | **Yellow** |

(4) **End-point :** The point or the stage at which the reaction is exactly completed in the process of titration (*e.g.* an acid is completely neutralised by a base or a base by an acid) is called the **end-point** (or **equivalence point**). It is made noticeable by the change of colour of the indicator used.

(5) **Neutralisation :** The reaction between an acid and a base, resulting in the formation of salt and water, is known as *neutralisation*. It is, in reality, a reaction involving the union

between $H^+$ ion(s) of an acid and $OH^-$ ion(s) of a base to form practically undissociated water molecule(s), as exemplified by,

$$\begin{array}{l}
\underset{\text{(acid)}}{HA} \xrightleftharpoons{\text{dissociation}} H^+ + A^- \\[1em]
\underset{\text{(base)}}{BOH} \rightleftharpoons OH^- + B^+ \\
\hline
HA + BOH \xrightarrow{\text{neutralisation}} \underset{\text{water}}{H_2O} + \underset{\text{salt}}{[B^+ + A^-]}
\end{array}$$

The process of neutralisation consists in mixing a solution of an acid with a solution of a base in such proportions that both of them are exactly reacted upon by each other and the resultant solution, after the reaction, contains neither an excess of the acid nor of the base, but contains only the products of the reaction, *viz.* salt and water.

(6) **Standard solution :** A standard solution is a solution of known strength, *i.e.* it is a solution which contains a known weight of the solute dissolved in a known volume of it.

(7) **Equivalent weight of an acid :** The equivalent weight of an acid is the number of parts by weight of the acid which contains 1·008 (or roughly 1·0) parts by weight (*i.e.* 1 atom or 1 equivalent) of replaceable hydrogen, or it is that part by weight of the acid which neutralises one equivalent of a base.

Thus, 36·5 parts by weight of hydrochloric acid [$HCl = 1 + 35{\cdot}5 = 36{\cdot}5$] contain 1 part by weight of replaceable hydrogen and hence, the equivalent weight of HCl is 36·5. Since the number of replaceable hydrogen atom(s) per molecule of an acid is its basicity, it follows that,

$$\textbf{Equivalent weight of an acid} = \frac{\textbf{Molecular weight of the acid}}{\textbf{Basicity}}.$$

(8) **Equivalent weight of a base :** The equivalent weight of a base is the number of parts by weight of the base that contains 17 parts by weight of replaceable hydroxyl group (OH), or it is that part by weight of a base which exactly neutralises one equivalent of an acid.

Thus, 40 parts by weight of sodium hydroxide [$NaOH = 23 + (16 + 1) = 40$] contain 17 parts by weight of replaceable hydroxyl group. So, the equivalent weight of NaOH is 40. The number of OH groups present per molecule of a base is known as its **acidity**. Therefore, it follows,

$$\textbf{Equivalent weight of a base} = \frac{\textbf{Molecular weight of the base}}{\textbf{Acidity}}.$$

The equivalent weights of a number of well-known acids and bases, along with their respective basicities (b) and acidities (a) and molecular weights are given in the table below :

| Name of the acid (formula) | b | Mol. wt | Eqv. wt | Name of the base (formula) | a | Mol. wt. | Eqv. wt. |
|---|---|---|---|---|---|---|---|
| Hydrochloric ($HCl$) | 1 | 36·5 | 36·5 | Sodium hydroxide ($NaOH$) | 1 | 40 | 40 |
| Nitric ($HNO_3$) | 1 | 63 | 63 | Potassium hydroxide ($KOH$) | 1 | 56 | 56 |
| Acetic ($CH_3COOH$) | 1 | 60 | 60 | Calcium hydroxide $[Ca(OH)_2]$ | 2 | 74 | 37 |
| Sulphuric ($H_2SO_4$) | 2 | 98 | 49 | Ammonium hydroxide ($NH_4OH$) | 1 | 35 | 35 |
| Oxalic (*anhyd.*) $[(COOH)_2]$ | 2 | 90 | 45 | | | | |
| Phosphoric ($H_3PO_4$) | 3 | 98 | 32·6 | | | | |

(9) **Equivalent weight of salts :** The equivalent weight of a salt is that part by weight of the salt which contains one equivalent of the positive ion (*i.e.* metallic or metal-like ion or radical). Since the number of equivalents of a metallic or metal-like ion is equal to its total valency, (*i.e.* valency × number of its ion present), the equivalent weight of a salt may be expressed as follows :

$$\text{Eqv. wt. of a salt} = \frac{\text{Molecular weight of the salt}}{\text{Total number of valencies of the positive ion(s).}}$$

Thus, the equivalent weight of $Na_2CO_3$

$$= \frac{2 \times 23 + 12 + 3 \times 16}{2 \times 1^{*}} = \frac{106}{2} = 53.$$

[*Since there are two sodium ions, and the valency of each sodium ion is 1.]

**(10) Gram-Equivalent weight or Gram-equivalent.**—The equivalent weight of a substance, when expressed in grams, is known as its gram-equivalent weight or gram-equivalent.

Thus, one gram-equivalent of $HCl = 36{\cdot}5$ grams HCl ;
one gram-equivalent of $NaOH = 40$ grams NaOH etc.

**(11) Strength (Concentration) of a solution.**—The strength (or concentration) of a solution always refers to the amount of the solute present in a known volume of it.

Since the amount of a solute may be expressed in different units, *e.g.* in **gms., gram-equivalents, gram-molecules** (or **moles**) **percent** etc., the strength of a solution may be accordingly expressed in different units, *e.g.* **gms./ml. or litre, Normality** (*i.e.* **gram-equivalents per** litre), **Molarity** (*i.e.* **moles per litre**) etc.

(a) **Normal solution : Normality.**—A normal solution of a substance is defined as the solution which contains one gram-equivalent of the substance in one litre of it.

The normality of a solution is, therefore, given by the number of gm-equivalents of the solute present per litre of the solution. It is designated by 'N'. Thus,

$$\text{Normality (N)} = \frac{\text{Number of gm-equivalents of the solute}}{\text{Number of litres of solution.}}$$

It, therefore, follows that, to prepare a normal solution of caustic soda [ eqv. wt. 40 ], for example, one has to dissolve 40 gms. of pure NaOH in 1 litre of distilled water.

Substances are, in practice, weighed in gms. Thus, if W gms. of a substance of eqv. wt. E are dissolved in L litres of water, the normality of the resultant solution maybe calculated as follows :

$$\text{Normality (N)} = \frac{W/E}{L} = \frac{W}{E} \times \frac{1}{L} = \frac{W}{L} \times \frac{1}{E} = \frac{W/L}{E}$$

$$= \frac{\text{amount in gms./litre}}{\text{Equivalent weight}}$$

$\therefore$ **Normality (N) × Equivalent weight**

**= amount in gms./litre.**

Thus, if an aqueous solution of KOH contains 100 gms. of the solute (KOH, eqv. wt. 56) in 2 litres of water, the normality of the solution will be calculated as :

$$\text{Normality (N)} = \frac{100}{56 \times 2} = \frac{25}{28} = 0{\cdot}893.$$

∴ The strength of the KOH solution = 0·893 (N).

If it is required to express the strength of this solution in gms./litre (or, if it is asked to calculate the amount of KOH in gms. present in one litre of this solution), then it can easily be done with the help of the above equation, *viz*,

Normality (N) × Equivalent weight = amount in gms /litre.

$$\therefore \text{ Amount of KOH} = 0{\cdot}893 \times 56 \text{ gms./litre}$$
$$= 50{\cdot}008 \text{ gms /litre}$$
$$\simeq \mathbf{50 \text{ gms./litre.}}$$

Normal solutions are, in general, found to be too concentrated to be used in volumetric analysis and so, more dilute solutions, *e.g.* semi-normal or decinormal solutions, or solutions of still lower concentrations are used.

**Decinormal solution.** $\left(\frac{N}{10} \text{ or } 0{\cdot}1N\right)$.—Decinormal solution of a substance refers to that solution which contains one-tenth of one gm-equivalent of the substance in one litre of it. Thus, a decinormal solution of NaOH contains $\frac{40}{10} = 4$ gms. of NaOH per litre of it. Similarly, semi-normal $\left(i.e. \frac{N}{2} \text{ or } 0{\cdot}5\ N\right)$, $\frac{N}{100}$ or, 0·01 N, $\frac{N}{1000}$ or 0·001 N, 1·5 N, 2N, 12N etc. solutions of a substance (say, NaOH) contain half the gm-equivalent (*i.e.* 20 gms. NaOH), one-hundredth of one gm-equivalent (*i.e.* $\frac{40}{100} = 0{\cdot}4$ gms. NaOH), one-thousandth of one gm-equivalent (*i.e.* $\frac{40}{1000} = 0{\cdot}04$ gms. NaOH), 1·5 times the gm-equivalent (*i.e.* $1{\cdot}5 \times 40 = 60$ gms. NaOH), 2 times the gm-equivalent (*i.e.* $2 \times 40 = 80$ gms. NaOH), 12 times the gm-equivalent (*i.e.* $12 \times 40 = 480$ gms NaOH) respectively, of the substance per litre of the solution.

**(b) Molar solution : Molarity.**—A molar solution of a substance is defined as a solution, a litre of which contains one gm-molecule (or, one *mole*) of the substance.

The molarity of a solution is, therefore, defined as the number of moles of the solute present per litre of the solution. It is designated by 'M'. Thus,

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Number of litres of solution}}.$$

To prepare a molar solution of $Na_2CO_3$ (mol. wt. 106), for example, one has to dissolve 106 gms. of pure sodium carbonate in 1 litre of distilled water. If instead of 106 gms., 140 gms. of $Na_2CO_3$ are dissolved in 1 litre of water, the molarity of the solution will then be calculated as :

$$\text{Molarity (M)} = \frac{\dfrac{140 \text{ gms.}}{\text{Mol. wt. of } Na_2CO_3}}{\text{Number of litres of water}} = \frac{\dfrac{140}{106}}{1} = 1{\cdot}321.$$

Or, the strength of the solution = 1·321 (M).

It follows from the above formulation that,

Molarity (M) × molecular weight = amount in gms./litre.

[For details of the other units of concentration (strength) of solutions, see "Poddar & Haldar—Higher Secondary Chemistry". vol. vol. I, § 10. ]

**Law of Normality.**—It follows from the very definitions of the equivalent weights of acids and bases that one equivalent of any acid completely reacts with (or neutralises completely) one equivalent of base (alkali). That is,

1 litre of N solution of an acid ≡ 1 litre of N solution of a base,

$\therefore$ 1 " " $\frac{N}{10}$ solution of acid ≡ 1 litre of $\frac{N}{10}$ solution of a base.

or, 25 ml. of $\frac{N}{10}$ solution of an acid ≡ 25 ml. of $\frac{N}{10}$ solution of a base.

From this, it can be generalised that *equal volumes of an acid and a base (an alkali) of the same strength (expressed in terms of normality) exactly neutralise each other.** This is known as the law of normality.

If 1 litre of N solution of an acid or an alkali is made to react with a weaker solution of an alkali or an acid respectively,

---

[*This generalisation does not, however, hold good if the strengths of acids and bases are expressed in terms of percentage.]

it is obvious, that a larger volume of the weaker solution will be required to react with a smaller volume of the stronger (*i.e.* an inverse proportion of their respective strength) for exact neutralisation. For example, if 1 litre (N) acid is to be neutralised by an alkali of decinormal strength, 10 litres of the latter will be required, since 1 litre of it contains only one-tenth of the gm-equivalent of the alkali and so, 10 litres only will contain 1 gm-equivalent of the alkali, which is required to exactly neutralise 1 gm-equivalent of the acid present in 1 litre of its (N) solution. Thus, it is seen that the volumes of an acid and an alkali required to exactly neutralise each other are in inverse proportion of their strengths, *i.e.*,

$$\frac{\text{volume of acid } (V_1)}{\text{volume of alkali } (V_2)} = \frac{\text{strength of alkali } (S_2)}{\text{strength of acid } (S_1)}$$

or, Volume of acid $(V_1) \times$ strength of acid $(S_1)$
$=$ volume of alkali $(V_2) \times$ strength of alkali $(S_2)$

or, $V_1 \times S_1 = V_2 \times S_2$.

This is the fundamental equation, known as the *Normality equation*, on which the calculations involving volumetric analysis are based.

**Reduction of any strength to normality.**

Basing on the Normality equation, it can be shown that,

$$1 \text{ ml. of } 1 \text{ (N) soln.} \equiv 10 \text{ ml. of } \frac{N}{10} \text{ soln.} \equiv x \text{ ml. of } \frac{N}{x} \text{ soln.}$$

or, $V \text{ ml. of } 1 \text{ (N) soln.} \equiv 10 \times V \text{ ml. of } \frac{N}{10} \text{soln.} \equiv x.\, V \text{ml. of } \frac{N}{x} \text{ soln. } \equiv \frac{V}{m} \text{ ml. of } m \text{ (N) soln.}$

or, $x$ ml. of $y$ (N) solution $\equiv (x \times y)$ ml. of (N) solution,
$\equiv y$ ml. of $x$ (N) solution.

(The sign $\equiv$ means "equivalent to.")

With the help of this generalised formulation, a solution of any strength can be expressed in terms of (N) solution.

Thus, V ml. of $x$ (N) solution $\equiv (V \times x)$ ml. of 1 (N) solution.

**Preparation of Normal and Decinormal solutions.**

To prepare a *normal* solution of a substance, one has to dissolve one gram-equivalent of the pure substance in one litre of distilled water. If, however, one-tenth of the gram-equivalent of the substance is dissolved is one litre of distilled water, a *decinormal* solution of the substance will be obtained.

**To Prepare a Decinormal Solution of Sodium Carbonate :**

**Principle.**—The equivalent weight of anhydrous sodium carbonate ($Na_2CO_3$) is 53. So, if $\frac{53}{10}$ gms. $=5{\cdot}3$ gms. of pure and dry $Na_2CO_3$ are weighed and dissolved in one litre of distilled water, a decinormal solution of $Na_2CO_3$ will result.

**Apparatus :** A balance, a volumetric flask (1 litre), a weighing bottle (more than half filled with pure, anhydrous $Na_2CO_3$), a wash bottle, a funnel, a glass rod and a dropper.

**Procedure :** (i) About 10 gms. of a pure and dry sample of sodium carbonate are taken into in a weighing bottle, which is accurately weighed along with its content. The required quantity (approximate) of sodium carbonate is transferred to the volumetric flask by placing a small dry funnel on its mouth, care being taken to see that not a speck of the $Na_2CO_3$ falls outside the funnel. The bottle along with the residual amount of sodium carbonate is weighed again and the difference in weights gives the weight of the sodium carbonate transferred.

(ii) Now, distilled water is carefully poured into the volumetric flask by washing down the funnel, at first in small quantities, to wash down the sodium carbonate completely from the funnel inside the flask. The inside of the funnel and its stem are carefully washed with distilled water by the jet of the wash-bottle and the washings are added to the contents of the flask. Thus, about half of the flask is filled with distilled water. The flask is now closed tightly with the stopper and well-shaken to completely dissolve all the solid. The stopper is then opened and distilled water is added through the jet of the wash-bottle to fill the flask upto the mark. The stopper is again closed and the solution shaken well for some time to make it uniform. [Care should be taken to see that the mark at the neck of the flask is not exceeded by the added water, and no liquid comes out while shaking the flask. It is advisable that the beginners should use a dropper to add water into the flask during the final stage of making up the volume.] The solution, thus prepared, should be kept well-stoppered after proper labelling.

If it is required to prepare **250 ml. or 500 ml.of $\frac{N}{10}$ solution of sodium carbonate,** the procedure is the same, except that one has to weigh

$$\frac{53\times 250}{1000\times 10}=1{\cdot}325 \text{ gms. or, } \frac{53\times 500}{1000\times 10}=2{\cdot}65 \text{ gms.}$$

of sodium carbonate respectively and dissolve the material in 250 ml. or 500 ml. of distilled water respectively, following exactly the same procedure as described above.

To prepare a **normal solution** of sodium carbonate, one has to weigh accurately 53 gms. of the material and dissolve it in 1 litre of distilled water in a 1-litre volumetric flask. If, however, **250 ml. of a normal solution** of sodium carbonate are to be prepared, one has to weigh $\frac{53}{4}=13{\cdot}25$ gms. of sodium carbonate and dissolve it in 250 ml. of water in a 250-ml flask.

**Normality factor.**—It is extremely difficult, or sometimes not possible, to weigh exactly the quantity of a substance required to prepare a standard solution of exact strength. For this reason, it is seldom attempted to weigh the exact amount of the substance required. The usual practice is to weigh a quantity of the substance, which may be a little less or a little more than the required amount, and then to dissolve the same in the required volume of water. The solution, thus obtained will not be exactly of the strength wanted, but will be of a little lower or of a little higher strength. In such cases, the strengths of the resultant solutions are expressed as a **fraction** (either smaller or greater than 1) of normal or decinormal strength, and this fraction is called the **normality factor.** It is calculated as the ratio of the amount of the substance taken (by weighing) to the exact amount required to prepare a solution of the given strength. Thus,

**Normality factor**

$$=\frac{\text{Amount of the substance taken by actual weighing}}{\text{The exact amount required}}.$$

**Example :** To prepare 1000 ml. of a decinormal solution of $Na_2CO_3$, the quantity required is 5·3 gms. If, however, by actual weighing, 5·368 gms. of $Na_2CO_3$ are taken and dissolved in a litre of water, the normality factor $= \frac{5·368}{5·30} = 1·013$.

∴ The strength of the solution prepared $= 1·013\left(\frac{N}{10}\right)$.

If it is required to prepare a solution of sodium carbonate of exactly $\left(\frac{N}{10}\right)$ strength, then it is necessary to adjust the volume of the solution prepared above to reduce its strength.

[See "Poddar & Haldar, Higher Secondary Chemistry", § 10.]

**To prepare a decinormal solution of $H_2SO_4$.**

The equivalent weight of sulphuric acid is 49. So, to prepare a decinormal solution, $\frac{49}{10} = 4·9$ gms. of pure (100%) sulphuric acid are to be dissolved in distilled water to make 1000 ml. But, the difficulty is that, the required quantity of acid cannot be weighed directly due to its highly hygroscopic nature. It is also not advisable to weigh such a corrosive and fuming liquid in a precision chemical balance. Further, the available acid is only of 95%—98% strength. So, it is measured in volumes, in a measuring cylinder, after knowing its density.

Let the acid taken be 98% pure and its density is 1·84 gms./ml.

Then 98 gms. $H_2SO_4$ are contained in 100 gms. of the acid supplied.

∴ 4·9 gms. $H_2SO_4$ are contained in $\frac{100 \times 4·9}{98} = 5$ gms. of the acid supplied.

Since the density of the acid is given to be 1·84 gms./ml., the volume of the given acid which contains 5 gms. of $H_2SO_4$ is $\frac{5}{1·84} = 2·72$ ml.

So, 2·72 ml. of the acid are to be measured out in a litre volumetric flask and water is added (*Carefully !*) to fill the flask up to the mark, when a decinormal solution of $H_2SO_4$ is expected to be obtained.

But, even then, the strength of this solution is approximate and not exact. It must be titrated against a standard solution of an alkali to determine its exact strength.

**Example.** —Let 20 ml. of this solution are exactly neutralised by 25 ml. of a 0·12 (N) solution of NaOH ; then the strength of the acid solution (say, S) is calculated as follows :

$$25 \text{ ml.} \times 0{\cdot}12 \text{ (N)} = 20 \times \text{S}.$$

$$\therefore \quad \text{S} = \frac{25 \times 0{\cdot}12}{20} \text{(N)} = 0{\cdot}15 \text{(N)}$$

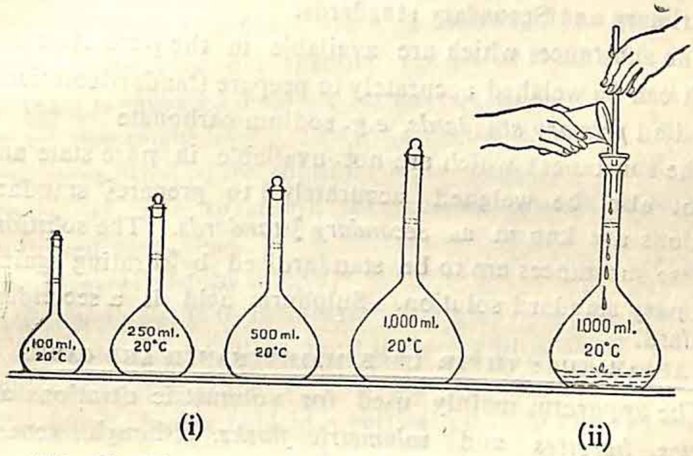


Fig. 7-1. (i) A few volumetric flasks of different sizes. (ii) The way of filling up a volumetric flask during preparation of solution.

If it is required to make this solution exactly decinormal, the volume should be adjusted.

**Preparation of a standard solution of lower strength from a more concentrated standard solution :** Let us suppose that we have a NaOH soln. of which the strength is 1·20 $\left(\frac{\text{N}}{10}\right)$. We are to prepare an exactly $\left(\frac{\text{N}}{10}\right)$ NaOH soln. from this stock soln. It is evident that the given soln. is to be diluted with water to certain extent so as to make it exactly $\left(\frac{\text{N}}{10}\right)$. The amount of water to be added may be calculated as follows :

Let $x$ ml. of water are to be added to 100 ml. of the stronger NaOH soln. to make it exactly $\left(\frac{\text{N}}{10}\right)$. So, the total volume of the diluted NaOH solution would be $(100+x)$ ml.

Hence, $(100+x)\frac{N}{10}=100\times 1\cdot 20\left(\frac{N}{10}\right)$

or, $100+x=100\times 1\cdot 20=120.$

or, $x=20.$

So, 20 ml. of water are to be added to each 100 ml. of $1\cdot 20\left(\frac{N}{10}\right)$ NaOH soln. to make it exactly $\left(\frac{N}{10}\right)$.

**Primary and Secondary standards.**

The substances which are available in the pure state and which can be weighed accurately to prepare standard solutions, are called *primary standards*, *e.g.* sodium carbonate

The substances which are not available in pure state and cannot also be weighed accurately to prepare standard solutions are known as *secondary standards.* The solutions of these substances are to be standardised by titrating against a primary standard solution. Sulphuric acid is a secondary standard.

## APPARATUS : THEIR USES, MAINTENANCE AND CARE.

The apparatus mainly used for volumetric titrations are *pipettes*, *burettes* and *volumetric flasks*, although general apparatus like conical flasks, beakers, clock glasses *etc.*, are also required for this purpose.

(1) **Pipette.**—A pipette is a glass tube with a cylindrical bulb in the middle, one end of the tube being drawn into a jet while the other stem carries a thin circular mark etched on it [Fig. 7-2(a)]. This mark indicates the volume of the liquid to be measured out by the pipette. This volume, *i.e.* the capacity of the pipette at a particular temperature, is usually engraved on the bulb. Pipettes of different capacities (2 ml., 5ml., 10ml., 25 ml., or 50 ml. *etc.*) are available, of which the pipettes of 10 ml. or 25 ml. capacities are generally used.

**The use of a pipette : Its cleansing and rinsing.**

Pipettes are *employed* for withdrawing a measured volume of a liquid accurately from a vessel and to transfer it to another.

The pipette must be *clean and free from grease* before use. For this purpose, the pipette is washed first with sodium carbonate solution then with dilute hydrochloric acid.* It is then washed thoroughly with distilled water and finally with absolute alcohol or acetone, which would not only remove grease but also help drying it quickly.

---

*It is often advised to use chromic acid (Pot. dichromate dissolved in conc. $H_2SO_4$) instead of hydrochloric acid.

The clean pipette is then rinsed once or twice with a little of the liquid which is intended to be measured.

To do this, a little of the solution is sucked by mouth into the pipette, the open end is closed immediately by the fore-finger. The pipette is now rotated in a horizontal position so that the whole internal surface is thoroughly washed. The liquid is then run out through the jet and discarded. The process is repeated again to ensure complete removal of any water that might have adhered inside the pipette. [It may be mentioned that, if the solution is to be *pipetted out* several times (as in a titration), this rinsing process need not be followed every time.]

**Measurement by a pipette.**—The given solution, of which a definite aliquot is to be measured out, is sucked by mouth into the pipette [Fig. 7-2(b) , until it rises a little above the mark. The open end is closed very quickly by the dry fore-fingure. The pipette is now held in a vertical position and the liquid is

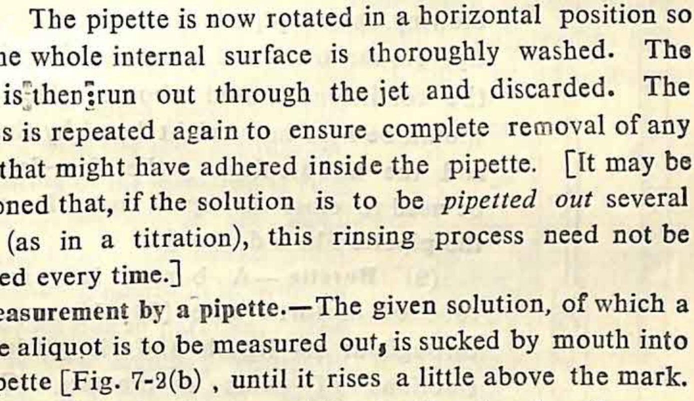


Fig. 7-2. (a) Pipettes of different sizes. (b) Sucking of liquid (or soln.) with the help of a pipette. (c) The method of transferring liquid (or soln.) from a pipette to a vessel.

allowed to run out slowly by slightly relaxing the pressure at the finger until the lowest point of the meniscus just coincides with the mark. Any error due to parallax is avoided by keeping the eye at the level of the lowest point of the meniscus. The liquid inside the pipette is then run out in a vessel (beaker or conical flask), by releasing the fore-finger and holding the pipette in a slightly inclined position, with its tip touched against the wall of the vessel, until the whole of the liquid is emptied. (It takes about 15 seconds) [Fig. 7-2(c)]. Any liquid, still remaining inside, need not be forced out by blowing, as the pipette is so calibrated that it delivers the measured quantity of liquid under the conditions stated above. [The pipette should be held in the right hand by the thumb and the middle-finger ; the fore-finger is to be used to close the open end. Do not hold the pipette like a dagger.]

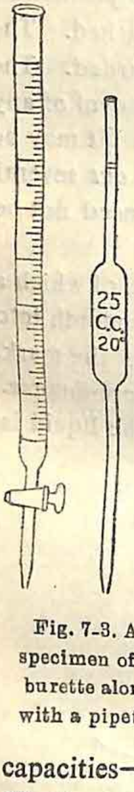


Fig. 7-3. A specimen of a burette along with a pipette.

(2) **Burette.**—A burette is a long glass tube of uniform bore (10—15 mm. diam.) throughout its length and is graduated in fractions of cubic centimeters. One end (upper) of the tube is open and the other (lower end is drawn to a jet and is fitted with a glass stop-cock about 5—6 cms. above the lowest jet-point. The graduation begins from a few centimeters below the upper end and goes downwards upto a few centimeters above the stop-cock, the uppermost graduation being marked 'zero', the lowermost graduation being marked according to the capacity of the burette. A burette may be of different capacities—25 ml., 50 ml ; 100 ml. *etc.*, of which a burette of 50 ml. capacity is generally used.

**The use of a burette : Its cleansing and rinsing.**

A burette is a very suitable apparatus for delivering variable volumes of a liquid contained in it, and the rate of delivery can be controlled by means of the stop-cock. It is, therefore, generally used for various types of titrations.

The burette must be cleansed and made grease-free before use, which may be done in the same way as described above for the cleansing of a pipette.

The clean burette is rinsed twice with the liquid with which the burette is to be filled, in the same way as the rinsing of a pipette.

**Measurement of the volume of a liquid by a burette.**

The burette is filled up with the solution (generally, acid solutions are taken in burette) to a little above the zero mark. The burette is held vertically and the liquid is allowed to flow out slowly by opening the stop-cock slightly, until the lowest point of the liquid meniscus just coincides with the zero graduation. **The position of the meniscus is read by placing the eye at the same horizontal level** as the lowest point of the concave meniscus in order to avoid errors due to parallax. The burette is now clamped vertically to a stand at a convenient height on the table. Particular care must be taken so that no air-bubble remains inside the jet or the burette. In such case, the stop-cock is fully opend and the liquid is allowed to run out with a force till the air-bubbles are expelled. The liquid is then poured in the burette to fill upto the zero mark again.

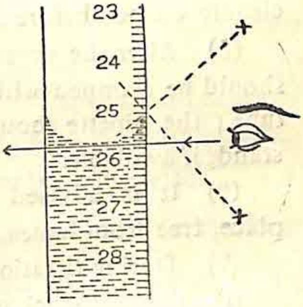


Fig. 7-4. Correct measurement of volume of liquid (or soln.) in a burette.

(3) **Volumetric flask.**—A volumetric flask is a flat-bottomed glass flask with a long narrow neck, fitted with a ground-glass stopper. The neck carries a thin circular mark etched on glass, which indicates the capacity of the flask. The capacity of a flask at a particular temperature is usually engraved on its wall. Flasks of different capacities—5 ml., 10 ml., 25 ml., 100 ml., 250 ml., 500 ml., 1000 ml., *etc.*—are available [See fig. 7-1 (i)].

Volumetric flasks are generally employed for preparing and storing standard solutions. Before use, the volumetric flasks must be cleansed properly to remove dirt and grease.

**General directions and precautions for the use, maintenance and care of the apparatus.**

(1) A burette should always be filled up with acid, and alkali should be taken in a beaker or a conical flask.

(2) Before starting an experiment, the stopper of the burette should be checked to see that it moves freely and does not leak. If required, it should be carefully greased.

(3) It is always safe to clamp the burette with a pad of paper round it.

(4) Burettes, pipettes and all other apparatus should be cleanly washed before and after the experiment.

(5) After the experiment, the clean and washed burette should be clamped with its jet upwards and covered by a test tube ; the pipette should be kept in a tall beaker or a pipette-stand, if available.

(6) It is advised to keep the apparatus in a clean dry place, free from fumes.

(7) During titration,

(i) the stop-cock of the burette should be carefully manipulated so that no liquid leaks out by its side,

(ii) parallax must be avoided at the time of noting the readings,

(iii) the burette should be filled every time up to the zero mark,

(iv) at least 3 titrations should be done with the same soln.,

(v) the burette or its jet must not contain any air-bubble,

(8) titre values differing by more than 0.5 ml. should not be taken into account.

## ACIDIMETRY

**Experiment-1.—Determination of the strength of an acid (sulphuric acid) with a standard alkali (sodium carbonate or caustic soda) solution, using methyl orange as indicator.**

**Principle.**—To determine strength of a solution of an acid ($H_2SO_4$), it is to be titrated in presence an indicator (methyl orange) against a solution of an alkali (NaOH) of known strength. The acid is taken in the burette and a known volume of the alkali solution is pipetted in out in a beaker (or conical flask) ; a little (∼2 drops) of the indicator is added and the alkali soluion is titrated by adding acid solution from the burette until the indicator just changes its colour.

If, $V_1$ (ml.) = the volume of acid solution required,
$V_2$(ml.) = volume of alkali taken,
$S_1$ = strength of the acid solutions (unknown),
$S_2$ = strength of alkali solution (known),

then, according to the law of normality,

$$V_1 \times S_1 = V_2 \times S_2$$

$$\text{or,} \quad S_1 = \frac{V_2 \times S_2}{V_1}$$

Now since $V_1$ (burette reading), $V_2$ (measured by pipette) and $S_2$ (given) are known, $S_1$ can be easily calculated.

Let the strength of the supplied* caustic soda (or sodium carbonate) solution be 1·025 $\left(\frac{N}{10}\right)$. With this solution, the strength of a given sulphuric acid solution (of unknown strength) is to be determined.

**Apparatus.**—Pipette (25 ml.), burette (50 ml.) conical flask (250 ml.), burette clamp and stand.

**Chemicals.**—The standard soln. of NaOH or $Na_2CO_3$; an aqueous solution of $H_2SO_4$, methyl orange soln. (*indicator*).

**Procedure.**—(i) The pipette, the burette and the conical flask are cleanly washed with distilled water.

(ii) The pipette is rinsed twice with the given caustic soda (or sodium carbonate) solution, and the washings are discarded. Then 25 ml. of the solution are pipetted out and delivered in the conical flask. About 20 ml. of distilled water are added to the alkali solution. [This will have no effect on the titration.]

(iii) The burette is rinsed twice with the given acid solution and is filled up to a little above the zero mark with the same acid solution. The acid solution is allowed to run down by opening the stop-cock of the burette to fill up the jet, leaving no air-bubble within it. If necessary, a little more of the acid solution is added to the burette and its level is made upto the zero mark.

---

*Standard solutions are to be supplied to the students.

(iv) Two drops of methyl orange indicator are added to the caustic soda (or sodium carbonate) solution taken in the conical flask, when the solution turns yellow.

(v) The conical flask with its content is placed beneath the burette. The stop-cock is opened and the acid solution is allowed to run out from the burette into the conical flask which is continuously shaken to mix the two liquids intimately (See fig 7-5). Care must be taken so that not a single drop of the acid solution falls outside the conical flask. After addition of about 15 ml. of the acid solution, the rate of addition is slowed down (1. ml. is added at a time), the mixture is shaken and the colour of the solution is observed. Near the *end-point* (**to be marked by the appearance of pink colour** in the vicinity where the acid-drop falls), the acid should be added drop by drop. The conical flask is shaken well and the addition of acid is continued until the **colour just changes from yellow to pink**, when the stop-cock is fully closed.

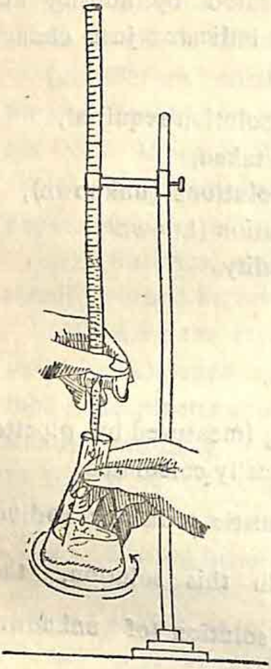


**Fig. 7-5.** The method of titration and handling of burette.

(vi) The burette-reading is observed to note down the volume of acid required to neutralise the sodium carbonate (or hydroxide) solution taken in the conical flask. This is a *trial* experiment and the results obtained need not be fully relied upon.

(vii) The burette is again filled upto the *zero* mark, the titrated solution (in the conical flask) is thrown into the sink, the conical flask is washed with distilled water and 25 ml. of the caustic soda (or sodium carbonate) solution are again pipetted out into the conical flask and the same operation of neutralisation is repeated thrice. It is to be mentioned that, during these titrations, the addition of the acid solution should be made rapidly upto 2—3 ml. less than the volume at which the end-point was obtained in the *trial* experiment above, and then it is added drop-wise till the change of colour just takes place from yellow to pink (in 1 drop = 0·05 ml ).

For instance, let the volume of acid required in the trial titration is 22·5 ml. ; in the subsequent titrations, 20 ml. of the acid solution should be added rapidly and then the rest should be added slowly and dropwise, till the yellow colour changes to pink by the addition of one drop of the acid solution. [It is helpful to place a piece of white paper below the conical flask during titration, so that the colour-change becomes prominent.].

**Results.**—The results of the titrations are presented in a table as shown below :

[The result of the *trial* titration is omitted.]

| No. of Experiments. | Volume of alkali soln. | Burette readings | | Volume of acid soln. required. | Mean volume of the acid soln. |
|---|---|---|---|---|---|
| | | initial | final | | |
| 1. | 25 ml. | 0 | 22·6 ml. | 22·6 ml. | |
| 2. | 25 ml. | 0 | 22·4 ml. | 22·4 ml. | 22·5 ml. |
| 3. | 25 ml. | 0 | 22·5 ml. | 22·5 ml. | |

So, 25 ml. of the alkali soln. ≡ 22·5 ml. of the acid soln.

**Calculation.**—From the law of normality.

Volume of the acid × Strength of the acid

= Volume of the alkali × Strength of the alkali.

Let the strength of acid soln. be S.

$$\therefore \quad 22{\cdot}5 \text{ ml.} \times S = 25 \text{ ml.} \times 1{\cdot}025 \left(\frac{N}{10}\right)$$

Or, $S = \frac{25 \times 1{\cdot}025}{22{\cdot}5}\left(\frac{N}{10}\right) = 1{\cdot}139\left(\frac{N}{10}\right)$.

∴ The strength of the acid soln. $= 1{\cdot}139\left(\frac{N}{10}\right) = 0{\cdot}1139(N)$

$= 0{\cdot}1139 \times 49$ gms./litre $= 5{\cdot}5811$ gms./litre.

(∵ the equivalent weight of sulphuric acid is 49.)

**Precautions.**—(i) Before use, burette and its stop-cock must be checked to see that the latter fits exactly into the former so that no leakage of solution would occur during titration..

(ii) Titrations should be done carefully so that stop-cock is not pushed forward which would cause leaking of acid solution and the whole titration would be spoiled.

(iii) Titrations should be done slowly (specially near the end point) by adding small quantity at a time, followed by shaking the titrate to avoid the danger of crossing the end point.

(iv) Parallax must be avoided during taking burette-reading.

## ALKALIMETRY

**Experiment-2. To determine the strength of NaOH solution with a standard $H_2SO_4$ solution, using phenolphthalein as indicator.**

**Principle.**—To determine the strength of a solution of an alkali (NaOH), it is to be titrated in presence of an indicator (say, phenolphthalein) against a solution of acid ($H_2SO_4$) of known strength. The acid is taken in the burette and the alkali solution pipetted out in a beaker (or a conical flask); a little (2 drops) of the indicator is added and the alkali solution is titrated by adding acid from the burette until the indicator just changes its colour. The volume of acid required is noted from the burette.

Let $V_1$ (ml.) = the volume of acid required,
$V_2$ (ml.) = the volume of alkali taken,
$S_1$ = strength of acid solution (known),
$S_2$ = strength of alkali solution (unknown).

Then, according to law of normality,

$$V_1 \times S_1 = V_2 \times S_2$$

$$\text{or, } S_2 = \frac{V_1 \times S_1}{V_2}.$$

Since $V_1$ (burette reading, $V_2$ (measured by pipette) and $S_1$ (given) are known, $S_2$ can be easily calculated,

Let the strength of the sulphuric acid solution be 1·01 $\left(\frac{N}{10}\right)$.

With this standard solution, an aqueous solution of sodium hydroxide is to be titrated and hence, the strength of the latter is to be determined.

**Apparatus.**—A pipette (25 ml.), a burette (50 ml.), a conical flask, a clamp and a stand.

**Chemicals.**—The standard solution of sulphuric acid, and aqueous solution of sodium hydroxide of unknown strength and phenolphthalein solution (*indicator*).

**Procedure.**—(i) The pipette is cleansed and then rinsed with the given caustic soda solution. 25 ml. of the caustic soda solution are pipetted out and transferred to a clean conical flask. The soln. is diluted with about 20 ml. of distilled water.

(ii) The burette is cleansed and then rinsed with the given acid solution. It is then filled up to the zero mark with the acid solution, after eliminating air-bubble, if any, within it. It is then clamped vertically to a stand.

(iii) 3—4 drops of phenolphthalein indicator are added to the caustic soda solution taken in the conical flask, when the colour of the solution turns pink.

(iv) The conical flask is now placed beneath the burette and the alkali solution is titrated against the acid solution, added from the burette in the same manner as described in the previous experiment (Expt.-1) upto the end-poind which is marked by the *change of colour from pink to colourless.* The burette-reading is noted.

(v) The procedure is repeated thrice with fresh aliquots (25 ml.) of the alkali soln. and the corresponding burette-readings are noted. During these subsequent titrations, the acid soln. should be added rapidly upto 2 ml. less than the volume required for complete neutralisation, (as indicated by the *trial* titration at the beginning), and the rest should be added dropwise with proper stirring, till the pink soln. changes to colourless by the addition of a single drop of the acid solution.

**Results.**—The results of titrations are presented in the table as shown below :

| No. of Experiments. | Volume of alkali pipetted out. | Burette readings | | Volume of acid required. | Mean Volume. |
|---|---|---|---|---|---|
| | | initial | final | | |
| 1 | 25 ml. | 0 | 21·8 | 21·8 ml. | 21·7 ml. |
| 2 | 25 ml. | 0 | 21·7 | 21·7 ml. | |
| 3 | 25 ml. | 0 | 21·6 | 21·6 ml. | |

So, 25 ml. of the alkali soln.≡21·7 ml. of the standard acid solution.

**Calculations.**—From the law of normality,

Vol. of acid $(V_1) \times$ strength of acid $(S_1)$

$= $ Vol. of alkali $(V_2) \times$ strength of alkali $(S_2)$

*i e.* $V_1 \times S_1 = V_2 \times S_2$.

In the present experiment,

$V_1 = 21{\cdot}7$ ml. ; $S_1 = 1{\cdot}01 \left(\frac{N}{10}\right)$ *(given)*

$V_2 = 25$ ml.

$\therefore$ So, $21{\cdot}7 \times 1{\cdot}01 \left(\frac{N}{10}\right) = 25 \times S_2$

or, $S_2 = \frac{21{\cdot}7}{25} \times 1{\cdot}01 \left(\frac{N}{10}\right) \approx 0{\cdot}877 \left(\frac{N}{10}\right)$

$\therefore$ The strength of the caustic soda solution

$= 0{\cdot}877 \left(\frac{N}{10}\right) = 0{\cdot}0877\ (N) = 0{\cdot}0877 \times 40$ gms./litre

$= 3{\cdot}508$ gms./litre, ($\because$ Eqv. wt. of caustic soda $= 40$)

**Precautions.**—Same as in Expt.-1.

***Equivalent weight of oxidising and reducing agents** — Equivalent weight of an oxidising or a reducing agent is expressed by the following relationship :

$$\text{Eqv. wt.}=\frac{\text{Mol. wt. of the oxidant (or reductant)}}{\text{no. of electrons which one molecule of the oxidant (or reductant) gains (or loses) in the reaction.}}$$

**Example :** Potassium permanganate is reduced in acid ($H_2SO_4$) medium by oxalic acid and is decolourised. The reaction is, $2KMnO_4+5(COOH)_2+3H_2SO_4=K_2SO_4+2MnSO_4+10CO_2+8H_2O.$

Potassium permanganate Oxalic acid* (anhydrous)

**Expressing this reaction in terms of two half-reactions involving electron-transfer :**

**reduction :** $MnO_4^-+8H^++5e=Mn^{+2}+4H_2O.$

**oxidation :** $2COO^- - 2e=2CO_2$

**Thus, the eqv. wt. of** $KMnO_4=\frac{\text{Mol. wt. of } KMnO_4}{5}$

$$\frac{39\cdot1+54\cdot9+4\times16}{2}=\frac{158\cdot0}{5}=31\cdot6$$

**and, the eqv. wt. of oxalid acid** $=\frac{\text{Mol. wt. of oxalic acid}}{2}$

$$=\frac{126}{2}=63.$$

*Formula of crystalline oxalic acid is $(COOH)_2$, $2H_2O$ and hence, its molecular weight $=(12+32+1)\times2+2\times18=126.$

**Preparation of $KMnO_4$ solution.**—potassium permanganate is not obtained in perfectly pure state. So, it cannot be weighed directly to prepare a standard solution. The solution of permanganate is not also stable ; it undergoes decomposition on standing. So, it connot be used as a *primary standard.*

To prepare approx. $\left(\frac{N}{10}\right)$ solution, about 3—3·2 gms. of potassium permanganate crystals are taken in a beaker and dissolved in 250 ml. distilled water (if necessary, by warming). The solution is then filtered through glass-wool set in a funnel which is placed at the mouth of a 1-litre volumetric flask. After complete filtration, the funnel is removed and the flask is filled up with distilled water up to the mark. It is stoppered, shaken well and stored in a cool, dark place.

**Preparation of standard oxalic acid solution.**—To prepare a standard oxalic acid solution of approximately $\left(\frac{N}{10}\right)$ strength, 1·5 to 1·6 gms. of pure crystaline oxalic acid, $(COOH)_2 . 2H_2O$, are accurately weighed, transferred to a 250 ml. volumetric flask and dissolved in distilled water. The flask is then filled up with distilled water upto the mark. It is stoppered, shaken well and stored.

**Standardisation of Potassium permanganate by oxalic acid**

**Principle.**—A solution of potassium permanganate may be standardised by titrating against a standard solution of oxalic acid, when the latter reduces the former, and the pink (or purple) colour of permanganate solution is discharged.

The reaction occurs suitably in acidic medium[$\sim$1(N) with respect to sulphuric acid.] and accurate results are obtained by titrating the oxalic acid soln. warmed to 60°–80°C, with constant stirring.

**Procedure :** (i) The burette is rinsed with the permanganate solution, filled up to the zero mark with the same permanganate solution and clamped vertically to a stand.

(ii) The pipette is rinsed with the standard oxalic acid solution and an aliquot of 25 ml. of the same solution is pipetted out to a clean beaker. To this are added 15-20 ml. of dilute sulphurie acid (1 : 4), and the mixture is diluted to about 200 ml. with distilled water. The beaker with its content is warmed to 80°C and the warm solution is titrated against potassium permanganate soln., at first slowly and then as rapidly as possible (to avoid cooling of the solution), with constant stirring with a glass rod. At the beginning, the colour of the permanganate soln. added does not discharge quickly. But, once the reaction starts, the colour of the added permanganate soln. is rapidly discharged. Near the end-point (marked by the slow rate of the discharge of permanganate colour), the permanganate soln. is added dropwise until with one drop, the whole mass of the liquid assumes a pink shade (the pink colour persists for 30 seconds, after which the colour may disappear). The stop-cock is fully closed and the burrette-reading is noted.

**N. B.** In the titration with permanganate soln., no indicator is used, since one drop of the titre soln. added in excess, imparts a good pink shade to the solution being titrated and the end-point can be distinctly observed.

Similar titrations may be repeated twice more and the burette-reading after each titration is noted.

**Results :** The results of titrations are presented as shown in the table below :

Let the strength of the standard oxalic acid soln. be $0{\cdot}8\left(\frac{N}{10}\right)$. [Given.]

| No. of titrations | Vol. of oxalic acid soln used | Burette readings | | Vol. of permanganate solution required | Mean volume |
|---|---|---|---|---|---|
| | | initial | final | | |
| 1 | 25 ml. | 0 | 20·0 ml. | 20·0 ml. | $\simeq$ 20·0 ml. |
| 2 | 25 ml. | 0 | 20·1 ml. | 20·1 ml. | |
| 3 | 25 ml. | 0 | 20·0 ml. | 20·0 ml. | |

So, 25 ml. of the standard oxalic acid soln. $\equiv$ 20·0 ml. of the permanganate soln.

**Calculation :** We know, $V_1 \times S_1 = V_2 \times S_2$

Here, $V_1$ = volume of oxalic acid soln. = 25 ml.

$S_1$ = strength of oxalic acid soln. = $0{\cdot}8\left(\frac{N}{10}\right)$ (given)

$V_1$ = volume of permanganate soln. = 20·0 ml.

$S_2$ = strength of permanganate soln, is to be calculated.

$$\text{So, } 25 \times 0{\cdot}8\left(\frac{N}{10}\right) = 20{\cdot}0 \times S_2$$

$$\text{or, } S_2 = \frac{25 \times 0{\cdot}8}{20{\cdot}0}\left(\frac{N}{10}\right) = 1\left(\frac{N}{10}\right)$$

## ORAL QUETIONS

1. What is acidimetry and how does it differ from alkalimetry ?

2. What is an end-point in a titration ? How is it characterised or marked ?

3. What is an indicator ? Name one indicator used in acid-base titration, mentioning its change of colour from acid to alkaline medium.

4. Why phenolphthalein is unsuitable as an indicator for titration of sodium carbonate with sulphuric acid ?

5. What do you mean by the acidity of a base and the basicity of an acid ?

6. How the equivalent weight of an acid (or base) is calculated ?

*7. What is redox titration ?

*8. How are the equivalent weights of oxidants and reductants calculated ?

9. What do you mean by primary or secondary standards ?

10. Is potassium permanganate a primary standard ? If not, why ?

# 8

# QUALITATIVE INORGANIC ANALYSIS

Chemical analysis of an inorganic substance includes (a) the identification of the elements or ions present in the substance together with its probable composition and (b) the estimation of the amounts of the different constituents of the substance. The first part of this analysis is dealt with in the branch of analytical chemistry, generally known as the *qualitative inorganic analysis*, and the second part in the *quantitative inorganic analysis*. In the present discussion, we shall give a general outline of the methods commonly employed in the qualitative inorganic analysis for the identification of some common metallic ions (or *cations*) and acidic ions (*anions*, essentially of mineral acids).

Before entering into the proper subject-matter, it is necessary to say a few words about the methods of analysis, and it is expected that the students should remember them properly so that this branch of chemistry does not turn out as a boring subject, causing unusual taxation on their memory. It is to be clearly understood that each and every observation we make in the course of an experiment of chemical analysis is the physical manifestation of some chemical processes undergoing within the system. Thus, the production of a colour, evolution of a gas or a smell, formation of a solid precipitate from a clear, transparent solution, or the dissolution of a solid, forming a clear liquid etc. during experiments are no magic which takes place *automatically* or without any rhyme or reason. Every observation we perceive through our senses during an experiment (e.g. the change of colour or the formation or dissolution of a solid, formation of gas-bubbles, by our eyes ; the evolution of a smell, by our nose ; the explosive decomposition of a substance, by our ears, or the formation of an oily or soapy solution, by our touch) is the outcome of some chemical reactions taking place in the test-tube or the beaker in which we are carrying out the experiment. So, in order to get a clear idea about the experiment, we should first know what are the actual chemical reactions that are taking place, and what are the products of such reactions. Such a knowledge will help in the correlation of the observed facts with the logical *inferences* or *conclusions* to be drawn from the experiment, without unnecessarily committing to memory the host of *observations* and their *inferences* given in the book. It is, therefore, necessary on the part of the students to know the chemistry involvod in any particular experiment, and throughout this book endeavour has been made to apprise the students of the chemical background or the theoretical basis of each experiment. These theoretical aspects are either already known to the students or they will learn them in their theoretical courses, and it is intended and essential that the students should make a proper combination of the theoretical and practical courses of the study to make it a composite or integrated one. Further, it is to be stressed that chemical analysis is not a matter of *chance* or *luck*. If the experiment is properly carried out according to the standard procedure, the correct result is bound to come, especially in the qualitative analysis, where the so-called *personal error* has little part to play. A student should keep his eyes, ears and nose open, together with his mind, and follow the instructions carefully while performing an experiment, and it is sure that he will get the correct result. He should not be biassed, or presume something without seeing the results of his experiment. Any presumption or biassedness has been found to draw wrong conclusions. Lastly, it should be advised that, while carrying out qualitative analysis, a student should take only a small pinch of his sample (about 0·05 gms.) for any experiment. This not only prevents wastage, but it helps to avoid unnecessary longer time required for completing the work of *Group Analysis* of metallic ions. It is assured that, a small pinch of sample is sufficient to arrive at the correct conclusions, provided the experiment is properly and carefully done.

**Indentification of inorganic ions or radicals.**

The inorganic substances that are included in the present study may be either a metallic salt of an inorganic acid or a metallic oxide. An oxide of a metal contains only the metal and oxygen ; as the detection of oxygen is not included in the course, the only ion to be detected in an oxide is the metal ion. A salt, however, is composed of two ions or radicals, *viz*, the metallic ion or the **basic radical** (cation) and the non-metallic ion or the **acid radical** (anion). [See also, Poddar & Haldar, *Higher Secondary Chemistry*, § 9.] So, both these radicals may be detected in such a sample. Cases may arise where the sample contains more than one radical of each type (either basic or acid). These may be indentified individually or there may be a necessity of separating the mixture and then testing for the individual ion. [The West Bengal syllabus, however, envisages that students are to identify **two** basic radicals in a mixture in one sample, and **one** acid radical in another *single* unknown salt sample. The basic radicals chosen are :

$Pb^{++}$; $Cu^{++}$, $Fe^{++}$, $Fe^{+++}$, $Al^{+++}$, $Zn^{+++}$, $Ca^{++}$ and $Mg^{++}$, while the acid radicals are $CO_3^{=}$, $Cl^-$, $S^=$, $SO_4^=$ and $NO_3^-$.

We shall, at first, proceed to give an account of the different tests of the above radicals individually. These tests are generally done in two ways—(i) the dry tests and (ii) the wet tests. In most of these cases (except a very few), definite chemical changes take place which will be described later.

(i) **The Dry Tests.**—In this process of testing, the solid sample is directly used to perform some experiments in order to get some ideas about its nature.

(ii) **The Wet Tests.** – In this process, the testing is carried out with the solution of the sample, either in water or in some acid.

It is to be remembered that the above two processes of testing are supplementary to each other. The dry tests generally give some preliminary ideas regarding the sample and no definite conclusion can be or should be drawn from them. The identity of the radical, as tentatively suggested by the results of the dry tests, should be *confirmed* by the wet tests (or preferably by a *special* or *specific* test, if available).

[It may sonetimes so happen that the finding of a dry test is not corroborated by a wet test ; in such cases, the *confirmatory* wet test is more dependable.]

Before carrying out the actual tests, some physical characteristics of the sample aretobe noted carefully and taken down in the note-book, as these often help in the correct indentification of the sample. These physical characteristics are :

(1) Colour of the sample (2) State of aggregation and (3) Solubility.

(1) *Colour :* Inorganic compounds have their characteristic colour, some of which are given below. From the colour of the sample under examination, some idea about its identity may be gathered.

| Metal ion | Oxide | Carbonate | Chloride | Sulphide | Sulphate | Nitrate |
|---|---|---|---|---|---|---|
| $Pb^{++}$ | PbO-yellow<br>$Pb_3O_4$-Red | White | White | Black | White | White |
| $Cu^{++}$ | Black | Green | Green | Black | Blue | Blue |
| $Fe^{++}$ | Black | White (unstable) | Green | Black | Green | Green |
| $Fe^{+++}$ | Brown | – | Yellow | Black | Yellow | Yellow |
| $Al^{+++}$ | White | – | White | – | White | White |
| $Zn^{++}$ | White | White | White | White | White | White |
| $Ca^{++}$ | White | White | White | White | White | White |
| $Mg^{++}$ | White | White | White | White | White | White |

*White* also includes *colourless.*

(2) *State of aggregation :* An inorganic sample (solid) may be crystalline or amorphous. Sometimes, a crystaline sample

may be supplied after powdering it finely and as such, they may be mistaken as an amorphous substance. In a mixture, however, one ingredient may be crystalline and the other amorphous or both of them may be crystalline or amorphous. Among the inorganic compounds, some have crystalline nature while others are amorphous and as such, this characteristic may help to identify them. For example. the following are crystalline : $CuSO_4$, $CuCl_2$. $FeSO_4$, $ZnSO_4$, $Al_2(SO_4)_3$ etc.; while $CaCO_3$, $ZnCO_3$, $MgCO_3$, PbS, HgS etc. are generally amorphous.

(3) *Solubility :* Solubility of an inorganic compound is a characteristic property of its own (see also, Poddar & Haldar, *Higher Secondary Chemistry*, §33). Some compounds are highly soluble in water, while some others are slightly soluble in water and some are not soluble at all in this solvent. Again, some inorganic salts are soluble in acids, either dilute or concentrated. These characteristics of inorganic compounds sometimes help in their identification and also lend added support to the correct finding of the experimenter. A simple illustration will show how important are the solubility data in the correct identification of a salt. Suppose, a white salt is found to be insoluble in water ; during the preliminary tests, and after carrying out all the dry and wet tests for the radicals, a student is ready to report his findings as lead nitrate. Now, lead nitrate is a white crystalline salt, easily soluble in water. So, the solubility of the unknown salt, which he has observed earlier, is in contradiction with his later findings regarding the radicals of the salt, and the student should pause for a while to think that there might have been some mistakes somewhere, either in finding the solubility of the salt in water or in detecting the correct radicals. Besides, the idea about solubility of the sample also helps the student in making solution of the same in the subsequent operations during *wet tests.*

## Dry Test of Basic Radicals

The following dry tests are generally carried out with the solid sample (finely powdered), in order of preference, to get some preliminary ideas regarding the basic radicals present in the salt :

(1) **Ignition Test or Heating in a dry test tube.** (2) **Charcoal-block Test** in (*a*) Oxidising flame without and with a drop of cobalt nitrate solution and (*b*) reducing flame. (3) **Flame Test**. (4) **Borax-bead Test.**

Another dry test, called the Soda-lime Test, is commonly done when ammonium salts are expected to be present in the sample.

**I. Ignition Test.**—A small quantity of the powdered sample is carefully transferred at the bottom of a hard-glass test tube, so that the salt does not adhere to the wall of the test tube. The test tube is then horizontally held over a Bunsen flame by means of a test tube holder (or a folded piece of paper). Temperature is gradually increased by heating, when any one or more of the following changes may occur and the changes are noted : (*a*) a sublimate is formed at the cooler part of the test tube, (*b*) the colour of the sample changes, (*c*) evolution of gases takes place and (*d*) the sample melts or decomposes with related external changes.

| *Observation* | *Inference* |
|---|---|
| (*a*) **A sublimate is formed.** | |
| (i) White sublimate. | May be ammonium halides, $HgCl_2$, $HgBr_2$, $Hg_2Cl_2$ or $As_2O_3$, $Sb_2O_3$. |
| (ii) Yellow sublimate. | $As_2S_3$, $HgI_2$ (becomes red on scratching with a glass rod). |
| (iii) Black sublimate. | HgS. |
| (*b*) **The substance changes colour.** | |
| (i) Blackens. | Cu, Ni and Mn salts at high temperature. |
| (ii) Yellow when hot, white when cold. | ZnO and many Zn-salts. |
| (iii) Yellowish-brown when hot, yellow when cold. | $SnO_2$ or $Bi_2O_3$. |
| (iv) Yellow when hot or cold. | PbO and some Pb-salts. |
| (v) Brown when hot or cold. | CdO and some Cd-salts. |
| (vi) Red to black when hot, brown when cold. | $Fe_2O_3$. |

| *Observation* | *Inference* |
|---|---|
| (*c*) **A gas is evolved with or without colour change.** | |
| (i) Water vapour is evolved (often with colour-change), | Compounds with water of crystallisation (or hydrated salts) |
| (ii) $O_2$ is evolved (re-kindles a glowing piece of wood) | May be nitrate. |
| (iii) $N_2O$ is evolved. | May be $NH_4NO_3$ (or a nitrate mixed with an ammonium salt). |
| (iv) Reddish-brown fumes ($NO_2$) are evolved. | May be nitrates (or nitrites) of heavy metals. |
| (v) $CO_2$ is evolved (tested by lime-water). | May be carbonates (or bicarbonates). |
| The colour of the residue (after evolution of $CO_2$) is yellow when hot, white when cold. | $ZnCO_3$. |
| The colour of the residue (after evolution of $CO_2$) is yellow when hot or cold. | $PbCO_3$. |
| The colour of the residue (after evolution of $CO_2$) is black. | $CuCO_3$. |
| (vi) $SO_2$ is evolved and a brown mass is left on strong heating. | May be $FeSO_4$. |
| (vii) $NH_3$ is evolved. | Ammonium salts. |
| (viii) Violet vapours of iodine are evolved. | May be some iodide. |

**Explanation :** (*a*) *Formation of sublimate.*—Many inorganic compounds sublime unchanged on heating, and a sublimate is formed at a cooler part of the test-tube. Ammonium halides, $HgCl_2$, $HgBr_2$, $Hg_2Cl_2$, $As_2O_3$ and $Sb_2O_3$ sublime on strong heating in the test tube and a white sublimate in each case is formed on the upper cooler part of the test tube.

When a white sublimate is formed, the sample may be heated with 4 times its volume of anhydrous $Na_2CO_3$ and a little KCN in a test tube. A grey mirror (changing to silvery globules on scratching with a glass rod) indicates Hg, a brownish-black mirror, giving a white sublimate and a garlic-like smell, indicates As, evolution of $NH_3$ indicates ammonium salts.

(*b*) *Colour-change on heating with or without evolution of a gas.*—Many salts of copper, nickel or manganese decompose into the corresponding oxides (black) when strongly heated and in many cases some gas is evolved.

$CuCO_3$ (bluish green) = $CuO$(black) + $CO_2\uparrow$;
$NiCO_3$ (bluish green) = $NiO$ (black) + $CO_2\uparrow$;
$PbCO_3 = PbO$ (yellow) + $CO_2\uparrow$;
$2Pb(NO_3)_2$ (white) = $2PbO$ (yellow) + $4NO_2$ (brown)$\uparrow$ + $O_2\uparrow$
$ZnCO_3$ (white) = $ZnO$ (white when cold, but yellow when hot) + $CO_2\uparrow$
$FeSO_4, 7H_2O$ (green) = $FeSO_4$ (white) + $7H_2O$ (steam)$\uparrow$;
$2FeSO_4 = Fe_2O_3$ (brown) + $SO_2\uparrow + SO_3\uparrow$.
$NH_4NO_3 = N_2O\uparrow + 2H_2O$ (steam)$\uparrow$.
$CuSO_4, 5H_2O$ (blue) = $CuSO_4$ (white) + $5H_2O$ (steam)$\uparrow$
$2CuSO_4 = 2CuO$ (black) + $2SO_2\uparrow + O_2\uparrow$.
$2HgO$ (red) = $2Hg$ (grey sublimate) + $O_2\uparrow$

**II. Charcoal-Block Test.**—A small quantity of the sample is taken in a small cavity of a charcoal-block and heated with a blow-pipe flame. [It sometimes happens to a young worker that a powdered sample kept in the charcoal cavity flies as the flame is blowed by the blow-pipe. In such cases, it is advisable to moisten the sample in the cavity with a drop of water before applying the flame jet.] The following observations may be made:

| *Observation* | *Inference* |
|---|---|
| (i) The substance decrepitates. | May be crystalline salts. |
| (ii) The substance catches fire (deflagrates). | May be nitrate. |
| (iii) The sample melts and is soaked in the charcoal-block. | May be salts of Na or K or of some alkaline earth metals. |

If during the above test, it is found that the sample does not melt (infusible), or it glows when blow-flame is applied on it (*i.e.* incandescent), or it forms an incrustation on heating, then a small quantity of the sample is well-mixed with twice its bulk of anhydrous $Na_2CO_3$ and the mixture is heated in the charcoal-block cavity with the reducing flame of the blow-pipe (§ 1). The following observations may be made :

| *Observation* | *Inference* |
|---|---|
| (i) White infusible mass, incandescent on heating. | BaO, CaO, SrO, MgO, $Al_2O_3$ ; ZnO. |
| (ii) An incrustation is formed but no metal is obtained. | |
| (*a*) White when cold yellow when hot | ZnO. |
| (*b*) Brown. | CdO. |
| (*c*) White with garlic-like smell. | $As_2O_3$ |
| (iii) A metal is obtained along with the formation of an incrustation. | |
| (*a*) White incrustation, brittle metal. | Sb |
| (*b*) Yellow ,, | Bi. |
| (*c*) ,, ,, malleable metal that marks paper. | Pb. |
| (iv) A metal is obtained, but no incrustation is formed. | |
| (*a*) Grey mass, attracted by magnet. | Fe, Ni, Co. |
| (*b*) Malleable bead. | Ag, Sn (white), Cu (red scales) |

**Test with cobalt nitrate solution.**—The white, infusible and incandescent mass in the above experiment is moistened with a drop or two of dilute cobalt nitrate solution and then strongly heated with the blow-pipe flame. Any colour-change of the sample is noted.

| *Observation* | *Inference* |
|---|---|
| (i) Blue mass (Thenard s blue) | $Al_2O_3$ |
| (ii) Green mass (Rinmann's green) | ZnO |
| (iii) Pink mass | MgO. |
| (iv) Grey mass | CaO (*not decisive*) |

N. B. It may be remembered that if much of cobalt nitrate solution is added, the heated sample turns black due to the formation of black cobalt oxide ($Co_3O_4$) which supresses the above characteristic colours.

**Explanation.**—The *decripitation* is due to the breaking down of the crystalline form of the sample. The *deflagration* on heating nitrates is due to the fact that, heating decomposes nitrates into $O_2$ or some oxides of nitrogen, which are strong supporters of combustion. These gases cause burning of the glowing charcoal-block

In the second series of tests, $Na_2CO_3$ converts the metallic salts into carbonates or oxides under the conditions of the experiments. The oxides are further reduced to the metallic state (wherever possible) by the reducing flame and the charcoal. Sodium carbonate acts as a flux and also protects the metals formed from oxidation. The *incrustations* are due to the oxides of the corresponding metals and, as such, have characteristic colours of the respective oxides. The infusible and incandescent mass, remaining after the experiments, are of the oxides of certain metals (BaO, SrO, CaO, MgO, $Al_2O_3$, ZnO), which are not reducible to the metallic stage under the conditions of the experiment.

The formation of the coloured mass during the third series of experiments is due to the formation of cobaltiates of Al, Zn and Mg,which have those characteristic colours Cobalt nitrate is first decomposed to cobaltous oxide (CoO) by heat ; this oxide then combines with the oxides of Al, Zn and Mg under the influence of heat, to form aluminium, zinc and magnesium cobaltiates.

$$2Co(NO_3)_2 = 2CoO + 4NO_2 + O_2,$$
$$Al_2O_3 + CoO = Al_2CoO_4 \text{ (Blue)},$$
$$ZnO + CoO = ZnCoO_2 \text{ (Green)},$$
$$MgO + CoO = MgCoO_2 \text{ (Pink)}.$$

**III. Flame Test.**—A clean platinum wire is dipped in conc. HCl taken in a watch-glass and then in the powdered sample. [A small quantity of the sample should be taken for this purpose in another watch-glass and after the test is completed this sample should not be used for testing acid radicals, especially *chloride.*] The moist sample at the tip of the platinum wire is then held at the base of the outer non-luminous flame of a Bunsen burner. Any development of characteristic colouration of the Bunsen-flame is noted.

| *Observation* | *Inference* |
|---|---|
| Strong and persistent golden-yellow | Na |
| Violet (lilac) | K |
| Brick-red (*transient*) | Ca |
| Crimson (*persistent*) | Sr |
| Yellowish-green (apple-green) | Ba |
| Green | Cu |
| Livid blue (with slow corrosion of platinum wire) | Pb, As, Sb, Bi. |

If sodium salts are present (even as small impurity), the strong golden-yellow flame invariably masks that of other elements, especially of potassium. In such cases, the coloured flame is observed through two thicknesses of cobalt-blue glass plates, when the colour of sodium-flame is absorbed (masked). The other colours are, however, somewhat modified by this procedure.

| *Original colour* | *Colour through blue glass* | *Inference* |
|---|---|---|
| Golden-yellow | Nil | Na |
| Violet | Crimson | K |
| Brick-red | Light-green | Ca |
| Crimson | Purple | Sr |
| Yellowish green | Bluish-green | Ba |

**Note :** It is essential that the platinum wire should be thoroughly cleaned before carrying out the test. As the test is a very sensitive one, any trace of colour-forming substance left in the wire (commonly from some previous experiments) may give erroneous results. The proper cleaning of a platinum wire may be done by repeated moistening with conc. HCl and subsequent burning in a Bunsen-flame, till no colouration of the flame is perceptible. A tenaciously adhering impurity may also be removed by cleaning the wire with molten borax or potassium bisulphate. For this purpose, the heated wire is dipped in some powdered borax or $KHSO_4$ and the wire with the adhered solid is heated on a flame when the solid melts. The molten solid is allowed to rinse the platinum wire by holding over the flame and giving a to-and-fro motion for some time. The molten salt is then thrown away and the platinum wire is cleaned by repeated moistening with conc. HCl and heating, till no colour is visible.

**Explanation :** The colour observed in the *Flame Test* is characteristic of the metal concerned. In order that the test should be successful, a volatile salt of the metal is needed. As the chlorides of metals are generally volatile on heating, these salts are used for the test. The sample is moistened with conc. HCl in order to transform it into chloride (if not already present as such).

$$CuCO_3 + 2HCl = CuCl_2 + CO_2 + H_2O,$$
$$Ca(NO_3)_2 + 2HCl = CaCl_2 + 2HNO_3.$$

If the given salt is already in the form of a chloride, the treatment with conc. HCl is not necessary. [Conc. HCl (instead of dil. HCl) is used to make the transformation easier.] Salts which are not soluble in conc. HCl (those salts which are not readily transformed to chlorides by the action of conc. HCl) do not readily give flame test. For example, $BaSO_4$ is practically insoluble and not easily affected by conc. HCl. So, the flame test is not responded to easily by this salt. Repeated moistening of this salt with conc. HCl and subsequent exposure to flame may give some positive indication of barium (as by such treatment a very small amount of $BaCl_2$ is formed). The best method of doing flame test with this salt is to reduce it by heating with charcoal powder (in a charcoal-block or in a hard-glass test-tube) to BaS and then to carry out the test with the reduced product (BaS) which easily forms $BaCl_2$ with conc. HCl.

[$BaSO_4 + 4C = BaS + 4CO$ ; $BaS + 2HCl = BaCl_2 + H_2S$.]

IV **Borax-bead Test.**—This test is to be carried out particularly with salts which are *coloured*, although colourless or white salts should also be subjected to this test [since $Mn^{+2}$ salts, e.g. $MnSO_4$, $MnCl_2$ etc. are so light-coloured (pink) that they appear to be almost colourless or white]. A small circular loop (about 2—3 mm. diameter) is made at the free end of the platinum wire. The loop is heated on a flame and it is dipped, while still red-hot, into powdered borax ($Na_2B_4O_7$, $10H_2O$) taken in a small watch glass. Some quantity of powdered borax will adhere to the loop, which is then heated on the flame until a colourless transparent bead is formed on the loop. A *very small* quantity of the salt-sample is taken on the bead by just touching the powdered sample by the hot bead. The bead with the sample is then heated in the outer oxidising flame of the burner and the colour of the bead is noted when it is hot and also when it is cold. The bead is then heated in the inner reducing flame of the burner and the colours are noted in the hot and cold conditions.

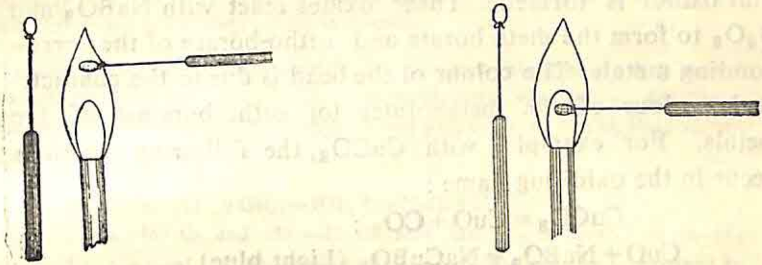


Fig. 8-1. Borax-bead tests : (a) in the oxidising flame and (b) in the reducing flame.

N.B. It is *essential* that a very small quantity of the sample should be taken for performing this test. If larger quantities of salt are taken, the bead becomes black.

**Colour of the borax-bead :**

| *Oxidising Flame* | | *Reducing Flame* | | *Inference* |
|---|---|---|---|---|
| Hot | Cold | Hot | Cold | |
| (i) Green | Blue | Red and opaque | Red and opaque | Cu |
| (ii) Yellowish brown | Yellow | Green | Green | Fe |
| (iii) Green | Green | Green | Green | Cr |
| (iv) Violet | Violet | Colourless | Colourless | Mn |
| (v) Blue | Blue | Blue | Blue | Co |
| (vi) Reddish brown | Reddish brown | Grey or black | Grey and opaque | Ni |

**Explanation** : Borax swells up on heating (loses water of crystallisation) and decomposes into sodium meta-borate ($NaBO_2$) and boron trioxide ($B_2O_3$) which from a transparent bead like glass.

$$Na_2B_4O_7 . 10H_2O = Na_2B_4O_7 + 10H_2O ;$$

$$Na_2B_4O_7 = \underbrace{2NaBO_2 + B_2O_3}_{\text{(Borax-bead)}} .$$

When a metallic salt is heated in the borax-bead test, the salt decomposes to the metallic oxide. In the oxidising flame, the higher oxide of the metal (i.e. the *-ic* oxide( is formed, while in the reducing flame, the lower oxide of the metal (i.e. the *-ous* oxide) is formed. These oxides react with $NaBO_2$ and $B_2O_3$ to form the meta-borate and ortho-borate of the corresponding metals. The colour of the bead is due to the characteristic colour of the metaborates (or ortho-borates) of the metals. For example, with $CuCO_3$, the following reactions occur in the oxidising flame :

$$CuCO_3 = CuO + CO_2\ ;$$

$$CuO + NaBO_2 = NaCuBO_3 \text{ (Light blue)}$$

(Sodium copper ortho-borate)

$$CuO + B_2O_3 = Cu(BO_2)_2 \text{ (blue)}$$

(Cupric meta-borate)

In the reducing flame, the cupric meta-borate is first reduced to colourless cuprous meta-borate and then to metallic copper, which is dull-red in colour,

$$2\ Cu(BO_2)_2 + C = Cu_2(BO_2)_2 + B_2O_3 + CO$$

(Cuprous meta-borate, colourless).

$$Cu_2(BO_2)_2 + C = 2Cu + B_2O_3 + CO$$

$$B_2O_3 + 2\ NaBO_2 = Na_2B_4O_7$$

In the case of an iron salt (ferrous or ferric), the heating in the oxidising flame produces $Fe_2O_3$ which ultimately forms *yellow* ferric meta-borate,

$$Fe_2O_3 + 3\ B_2O_3 = 2\ Fe(BO_2)_3 \text{ (yellow)}$$

(Ferric meta-borate)

In the reducing flame, ferric meta-borate is reduced to *green* ferrous meta-borate,

$$2\ Fe(BO_2)_3 + C = 2\ Fe(BO_2)_2 + B_2O_3 + CO$$

(Ferrous meta-borate, green)

$$B_2O_3 + 2NaBO_2 = Na_2B_4O_7.$$

Manganese salts form manganic meta-borate (violet) in the oxidising flame and this is reduced to manganous meta-borate (colourless) in the reducing flame. Chromium and cobalt salts form in the oxidising flame, green chromic meta-borate, $Cr(BO_2)_3$ and blue cobaltous meta-borate, $Co(BO_2)_2$

(cobaltic meta-borate is not formed). Chromic meta-borate is not reduced in the reducing flame. So, in the cases of chromium and cobalt salts, the same colour of the bead is produced in both oxidising and reducing flames. In the case of nickel salts, the NiO formed in the oxidising flame produces brown $Ni(BO_2)_2$. In the reducing flame, the $Ni(BO_2)_2$ is reduced to metallic nickel and as such, an opaque bead is formed.

**Test for Ammonia : Soda-Lime Test.**—An ammonium salt, when heated with soda-lime (or with NaOH soln.) produces ammonia (gas). Ammonia is detected by its smell and its action on red litmus paper (turns *blue*) or on Nessler's solution.

$$NH_4Cl + NaOH\ (+CaO) = NH_3\uparrow + NaCl + H_2O,$$

**Special Tests for Cr and Mn.**—If Cr and Mn are suspected from the borax-bead or charcoal test, the following experiment may be performed in order to be sure of their presence :

A little quantity of the sample is mixed with anhydrous $Na_2CO_3$ and $KNO_3$, and the mixture is fused on a platinum foil (or a mica-foil or a broken piece of porcelain). A *green* mass on cooling indicates Mn and a *yellow* mass indicates chromium. The green mass is dissolved in water, filtered and the filtrate is acidified with dil. $HNO_3$. A *pink* colour is developed, which confirms Mn. On the other hand, the yellow mass is dissolved in water and filtered. The filtrate is acidified with dil. acetic acid and boiled to expel $CO_2$ (if any) and then treated with lead acetate solution. A *yellow* precipitate confirms Cr.

On heating with $Na_2CO_3$ and $KNO_3$, the manganese and chromium salts are first decomposed into MnO and $Cr_2O_3$ respectively. These oxides then react with $Na_2CO_3$ in presence of $O_2$ (aerial or from $KNO_3$) to form *green* sodium manganate ($Na_2MnO_4$) and *yellow* sodium chromate ($Na_2CrO_4$) respectively. Green $Na_2MnO_4$ is subsequently acidified with dil. $HNO_3$ when *purple* sodium permanganate ($NaMnO_4$) is formed. On the other hand, the solution of sodium chromate forms a yellow precipitate of lead chromate ($PbCrO_4$), insoluble in dil. acetic acid, on treatment with lead acetate.

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 = 4Na_2CrO_4 + 4CO_2.$$
$$MnO + Na_2CO_3 + O_2 = Na_2MnO_4 + CO_2.$$
$$Na_2CrO_4 + Pb(CH_3COO)_2 = PbCrO_4\downarrow + 2CH_3COONa.$$
$$3Na_2MnO_4 + 2H_2O = 2NaMnO_4 + MnO_2 + 4NaOH.$$

## Wet tests for Individual Basic Radicals.

In order to carry out the wet tests for basic radicals, the solid sample is to be brought into a clear, transparent solution, either by dissolving in water (cold or hot) or in dilute HCl (cold or hot). [The syllabus includes only those samples which are soluble in water or dilute hydrochloric acid.]

**Preparation of Solution.**—A small quantity (about 0·2—0·3 gms.) of the solid sample (finely powdered) is taken in a test tube or a small beaker and about 15 ml. of distilled water are added to it. The mixture is shaken well or stirred well with a glass rod. If the solid sample completely dissolves, giving a clear solution, then the tests maybe carreid out with it. It may, however, so happen that most of the solid goes into solution, leaving a small quantity undissolved ; then try to dissolve the rest by adding a little more water. In case the sample seems to be mainly remaining undissolved, heat the mixture over a flame and observe if solution is effected. [There are some solids which are slightly soluble in water at ordinary temperatures, but dissolve completely in hot water ] To get an idea whether the sample has gone into solution or not, it is advisable to keep the mixture, after theabove operations, undisturbed for sometime. If the solid has not dissolved, it will gradually settle at the bottom of the test tube or the beaker. [There are some compounds like lead chloride ($PbCl_2$) which are quite soluble in hot water, but are sparingly so in cold water, and in these cases, the solid salt precipitates on cooling the solution. In such cases, the solution may be made by using a small quantity of the salt and excess of water and the tests are preferably carried out when the solution is still warm. There are other samples like calcium sulphate (or even sodium sulphate) whose solubilities in water decreases with the rise of temperture.] If the sample is not soluble in water (cold or hot), it should be dissolved in dilute hydrochloric acid, either at ordinary temperature or by heating (in order of preference). As already stated, it is desirable that the solution of the sample for wet analysis should be clear and transparent. But, it sometimes happens in practice that the prepared solution is somewhat *hazy* in appearance, although no visible precipitate settles down. This may be due to the presence of some insoluble impurities in the sample and such a solution should be filtered before use.

## Reactions of the Lead Ion ($Pb^{++}$)

*Used an aqueous solution of lead acetate or lead nitrate.*

Taken about 2 ml. of the solution in a test tube to carry out the following tests :

| *Experiment* | *Observation* | *Inference with explanation* |
|---|---|---|
| 1. Added dil. HCl. | A white precipitate is formed, which is soluble on heating, but separates out again as white needles when the solution is cooled. | Lead chloride ppt. ($PbCl_2$) is formed in the cold and this is soluble in hot water.<br>$Pb(NO_3)_2 + 2HCl = PbCl_2 + 2HNO_3$ |
| 2. Added potassium iodide solution. | A yellow precipitate is formed. The precipitate is moderately soluble on boiling to give a colourless solution, from which golden yellow flakes are precipitated on cooling. The precipitate is also soluble in excess of KI soln. | Yellow lead iodide ($PbI_2$) is formed. $PbI_2$ is soluble in excess KI soln. to give a complex salt, $K_2[PbI_4]$.<br>$Pb(NO_3)_2 + 2KI = PbI_2 + 2KNO_3$.<br>$PbI_2 + 2KI = K_2[PbI_4]$ |
| 3. Added dil. $H_2SO_4$. | A white ppt. is formed. The ppt. is insoluble in excess $H_2SO_4$, but is soluble in concentrated ammonium acetate soln. | White lead sulphate is formed, which is insoluble in $H_2SO_4$, but soluble in ammonium acetate soln. due to the formation of lead acetate.<br>$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3$.<br>$PbSO_4 + 2NH_4.C_2H_3O_2 = Pb(C_2H_3O_2)_2 + (NH_4)_2SO_4$. |

| *Experiment* | *Observation* | *Inference with explanation* |
|---|---|---|
| 4. Added potassium chromate soln. | A yellow ppt. is formed. The ppt. is insoluble in acetic acid and $NH_4OH$, but soluble in NaOH soln. and in $HNO_3$. | Yellow lead chromate ($PbCrO_4$) is formed, which is insoluble in acetic acid. The ppt. dissolves in NaOH soln. and $HNO_3$ to form sodium plumbite, ($Na_2PbO_2$) and $Pb(NO_3)_2$ respectively.<br>$PbCrO_4 + 4NaOH = Na_2PbO_2 + Na_2CrO_4 + 2H_2O$.<br>$PbCrO_4 + 2HNO_3 = Pb(NO_3)_2 + H_2CrO_4$. |
| 5. Passed $H_2S$ gas through the soln. | A black ppt. is formed. The ppt. is insoluble in dil. HCl, but soluble in hot dil. $HNO_3$, with the precipitation of sulphur. | Black lead sulphide (PbS) is formed. PbS is insoluble in dil. HCl, but soluble in hot dil. $HNO_3$.<br>$Pb(NO_3)_2 + H_2S = PbS + 2HNO_3$.<br>$3PbS + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O + 3S$. |
| 6. Added NaOH soln. | A white ppt. is fermed, which dissolves on adding excess NaOH soln. | White lead hydroxide [$Pb(OH)_2$] is formed. $Pb(OH)_2$ dissolves in excess NaOH soln., forming sodium plumbite, $Na_2PbO_2$.<br>$Pb(NO_3)_2 + 2NaOH = Pb(OH)_2 + 2NaNO_3$.<br>$Pb(OH)_2 + 2NaOH = Na_2PbO_2 + 2H_2O$. |

### **Reactions of Copper (ic) ion ($Cu^{++}$)**

Used an aqueous solution of Copper sulphate(~2ml.) to carry out the following tests :

| *Experiment* | *Observation* | *Infererence with explanation* |
|---|---|---|
| 1. Passed $H_2S$ through the soln., acidified with dil. HCl. | A black ppt. is formed. The ppt. is soluble in hot dil. $HNO_3$, but insoluble in boiling dil. $H_2SO_4$.<br>(*Distinction from Cd*) | Black copper sulphide (CuS) is formed. CuSis soluble in hot dil. $HNO_3$, with the precipitation of sulphur.<br>$CuSO_4+H_2S = CuS + H_2SO_4$.<br>$3CuS + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO + 2S$ |
| 2. Added NaOH soln. | A blue ppt. is formed. The ppt. is insoluble in excess of NaOH soln., and becomes black on boiling. | Blue copper hydroxide [$Cu(OH)_2$] is formed, which is insoluble in caustic soda soln , but is converted into black cupric oxide (CuO) on boiling.<br>$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4$<br>$Cu(OH)_2 = CuO + H_2O$. |
| 3. Added $NH_4OH$ soln. | At first a pale blue ppt. is formed, which dissolves in excess of ammonium hydroxide to give a deep blue soln. | At first, the pale blue ppt. of the basic salt, $CuSO_4$, $Cu(OH)_2$ is formed. This basic salt is soluble in excess of $NH_4OH$, giving a deep blue soln. of cuprammine sulphate, $[Cu(NH_3)_4]SO_4$.<br>$2CuSO_4 + 2NH_4OH = CuSO_4, Cu(OH)_2 + (NH_4)_2SO_4$.<br>$CuSO_4, Cu(OH)_2 + (NH_4)_2SO_4 + 6NH_4OH = [Cu(NH_3)_4]SO_4 + 8H_2O$. |

| *Experiment* | *Observation* | *Inference with Exaplanation* |
|---|---|---|
| 4. Added potassium ferrocyanide, $K_4[Fe(CN)_6]$, soln. | A chocolate-brown ppt. is formed. The ppt. is insoluble in dil. acids, but soluble in $NH_4OH$, forming a deep blue soln. | A chocolate-brown ppt. of cupric ferrocyanide, $Cu_2[Fe(CN)_6]$ is formed. This is insoluble in dil. acids, but dissolves in $NH_4OH$, forming complex copper ammine.<br>$2CuSO_4 + K_4[Fe(CN)_6] = Cu_2[Fe\,CN_6)] + 2K_2SO_4$. |
| 5. Dipped a clean iron-strip in the soln. | A red deposit is formed on the iron strip. | Iron displaces Cu from copper sulphate soln., and metallic copper deposits on iron.<br>$CuSO_4 + Fe = FeSO_4 + Cu \downarrow$ |

### Reactions of Ferrous ion ($Fe^{++}$)

Used aqueous solution of ferrous ammonium sulphate (*Mohr's Salt*), $FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$ or $FeSO_4$, $7H_2O$ (Green Vitriol) (∽2ml.) to carry out the following tests :

| *Experiment* | *Observation* | *Inference with Explanation* |
|---|---|---|
| 1. Added NaOH soln. | A greenish white ppt. is formed. The ppt. turns brown on exposure to air. | Greenish white ppt. of ferrous hydroxide, $Fe(OH)_2$, is formed. The colour of the ppt. turns brown on exposure to air due to the oxidation to brown ferric hydroxide.<br>$FeSO_4 + 2NaOH = Fe\,OH)_2 \downarrow + Na_2SO_4$.<br>$4Fe\,OH)_2 + 2H_2O + O_2 = 4Fe(OH)_3$. |

| *Experiment* | *Observation* | *Inference with Explanation* |
|---|---|---|
| 2. Added $NH_4OH$ soln. with or without adding excess of $NH_4Cl$ soln. | A greenish white ppt. is formed in absence of $NH_4Cl$. But, no ppt. is formed when excess of $NH_4Cl$ is added prior to the addition of $NH_4OH$. | Greenish white ppt is of $Fe(OH)_2$ is formed in absence of $NH_4Cl$. The presence of excess of $NH_4Cl$ hinders the precipitation of $Fe(OH)_2$ due to common-ion effect. (See Poddar & Haldar *Higher Secondary Chemistry*, § 33 )<br>$FeSO_4 + NH_4OH = Fe(OH)_2 + (NH_4)_2SO_4$<br>The ppt. of $Fe(OH)_2$ turns brown in air, as stated above. |
| 3. Passed $H_2S$ into the solution acidified with dil. $H_2SO_4$. | No ppt. | No Ferrous sulphide is pptd., as it is soluble in acid solution. |
| 4. Added ammonium sulphide soln. | A black ppt. is formed. The ppt. is soluble in dil. mineral acids, and turns brown on exposure to air. | The black ppt., of ferrous sulphide (FeS) is formed in neutral or ammoniacal medium. FeS is soluble in dil. mineral acids, and is oxidised to basic ferric sulphate, $Fe_2O(SO_4)_2$; on exposure to air.<br>$FeSO_4 + (NH_4)_2S = FeS \downarrow + (NH_4)_2SO_4$.<br>$FeS + 2HCl = FeCl_2 \times H_2S$. |

| *Experiment* | *Observation* | *Inference with Explanation* |
|---|---|---|
| 5. Added potassium ferrocyanide, $K_4[Fe(CN)_6]$, soln. | In absence of air, a white ppt. is formed; under ordinary atmospheric conditions, a pale blue ppt. is obtained. | The white ppt. is of **ferrous ferrocyanide** $Fe_2[Fe(CN)_6]$; or of potassium ferrous **ferrocyanide,** $K_2Fe[Fe(CN)_6]$.<br>The composition of the ppt depends upon the relative amounts of the salt soln. taken and the reagent added. Ferrous ferrocyanide undergoes partial oxidation to blue potassium ferric ferrocyanide, $KFe[Fe(CN)_6]$ (Prussian blue). $FeSO_4 + K_4[Fe(CN)_6] = K_2Fe[Fe(CN)_6] + K_2SO_4$. |
| 6. Added potassium ferricyanide $K_3[Fe(CN)_6]$ soln. | Dark blue ppt. is formed. | The dark blue ppt. is of **Potassium ferrous ferricyanide,** $KFe[Fe CN)^6]$ (*Turnbull*'s *blue*).<br>$FeSO_4 + 2K_3[Fe(CN)_6] = KFe[Fe(CN)_6] + K_2SO_4$. |
| 7. Added ammonium thiocyanate soln. | No colouration is obtained. (Distinction from $Fe^{+++}$.) | Ammonium thiocyanate (also called ammonium sulphocyanide) does not react with ferrous ion. But, this is a very sensitive test. Any trace impurity of ferric salt in the ferrous salt (sample) may give a positive test. |

| *Experiment* | *Observation* | *Inference with Explanation* |
|---|---|---|
| 8. Boiled with 1-2 drops of conc. $HNO_3$. | The green colour of the soln. changes to yellow. | Ferrous salts are green in colour. Conc. $HNO_3$ oxidises ferrous ion to ferric ion, whose colour is yellow.<br>$3FeSO_4 + 4HNO_3$<br>$= Fe_2(SO_4)_3$<br>$+ Fe(NO_3)_3 + NO$<br>$+ 2H_2O$ |

---

**Reactions of Ferric ion ($Fe^{+++}$)**

Used a solution of $FeCl_3, 6H_2O$, acidified with a little HCl (to prevent hydrolysis).

| *Experiment* | *Observation* | *Inference with Explanation* |
|---|---|---|
| 1. Added sodium hydroxide soln. | Reddish brown ppt., insoluble in excess of the reagent, but soluble in dil. mineral acids. (Distinction from Al and Cr.) | Reddish brown ppt. of ferric hydroxide, $Fe(OH)_3$, is formed. The ppt. is insoluble in NaOH soln, but soluble in mineral acids.<br>$FeCl_3 + 3NaOH$<br>$= Fe(OH)_3 \downarrow$<br>$+ 3NaCl.$<br>$Fe(OH)_3 + 3HCl$<br>$= FeCl_3 + 3H_2O.$ |
| 2. Added $NH_4OH$ soln. | Same as above. | $FeCl_3 + 3NH_4OH$<br>$= Fe(OH)_3$<br>$+ 3NH_4Cl.$<br>$Fe(OH)_3 + 3HCl$<br>$= FeCl_3 + 3H_2O.$ |

| *Experiment* | *Observation* | *Inference with Explanation* |
|---|---|---|
| 3. Passed $H_2S$. | The yellow colour changes to green and a yellowish white ppt. is formed. | Ferric sulphide, $Fe_2S_3$ is *not* formed in acidic soln. Ferric salt is reduced by $H_2S$ to ferrous salt (green), with the separation of sulphur.<br>$2FeCl_3+H_2S = 2FeCl_2+2HCl + S\downarrow$. |
| 4. Added ammonium sulphide soln. | A black ppt. is formed. The ppt. dissolves in dil. HCl, forming a green soln. and a yellowish white ppt. | The black ppt. is of $Fe_2S_3$ which is formed in ammoniacal medium. The ppt. dissolves in dil. HCl, forming $FeCl_2$ (green) and precipitating sulphur.<br>$2FeCl_3+3(NH_4)_2S = Fe_2S_3+6NH_4Cl$.<br>$Fe_2S_3+4HCl = 2FeCl_2+2H_2S\uparrow + S\downarrow$. |
| 5 Added potassium ferrocyanide soln. | A deep blue ppt. is formed. | Deep blue ppt. of potassium ferric ferrocyanide (*Prussian blue*) is formed.<br>$FeCl_3 + K_4[Fe(CN)_6] = KFe[Fe(CN(_6] + 3KCl$. |
| 6. Added potassium ferricyanide soln. | A brown coloration is formed. | Brown ferric ferricyanide *is* formed in solution.<br>$FeCl_3+K_3[Fe(CN)_6] = Fe[Fe(CN_6] + 3KCl$. |

| *Experiment* | *Observation* | *Inference with Explanation* |
|---|---|---|
| 7. Added ammonium thiocyanate soln. | A deep red coloration is produced. The colour is extractible with ether and is discharged by $HgCl_2$ soln. (Distinction from Ferrous ion.) | The blood-red colour is due to the formation of ferric ferrithiocyanate, $Fe[Fe(CNS)_6]$.<br>$2FeCl_3 + 6NH_4CNS \rightleftharpoons Fe[Fe(CNS)_6] + 6NH_4Cl$. |

### Distinction between Ferrous and Ferric salts.

Ferrous salts are generally green coloured, while the ferric salts are yellow to yellowish brown in colour (except sulphides, which are black in both the cases). The distinctive tests are as follows:

| *Reagent* | *Ferrous salt* | *Ferric salt* |
|---|---|---|
| 1. Potassium ferrocyanide soln. | White or pale blue ppt. | Deep blue ppt. **(Prussian blue)** |
| 3. Potassium ferricyanide soln. | Deep blue ppt. **(Turnbull's blue)** | No ppt. |
| 3. Ammonium thiocyanate soln. | No coloration in complete absence of ferric salt. | Deep red coloration, discharged by mercuric chloride soln. |
| 4. Ammonium hydroxide soln. | White to greenish white ppt., gradually changing to brown on exposure to air. | Reddish brown ppt. |

### Reaction of Aluminium ion ($Al^{+++}$)

Used a solution of aluminium sulphate, $Al_2(SO_4)_3, 18H_2O$, acidified with a little dil. $H_2SO_4$ (to avoid hydrolysis).

| *Experiment* | *Observation* | *Inference with explanation* |
|---|---|---|
| 1. Added $NH_4OH$ soln. | A gelatinous white ppt. is formed, which is *practically* insoluble in ammonia or $NH_4Cl$ soln., but is soluble on boiling with NaOH soln. The ppt. is also soluble in dil. HCl. | The white gelatinous ppt. is of aluminium hydroxide which is insoluble in ammonia, but soluble in hot NaOH soln., forming sodium aluminate in soln.<br>$Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3 + 3(NH_4)_2SO_4$.<br>$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$.<br>$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$. |
| 2. Added NaOH soln. | A gelatinous white ppt. is formed. The ppt. is soluble in excess of the reagent and also in dil. HCl. | The ppt. is of $Al(OH)_3$. The other reactions of the ppt. are the same as stated above. |
| 3. Added ammonium sulphide soln. | A white gelatinous ppt. is formed. | The ppt. is of $Al(OH)_3$ and has the same properties as stated above. Aluminium sulphide is completely hydrolysed in water and thus $Al(OH)_3$ results.<br>$Al_2S_3 + 6H_2O = 2Al\ OH)_3 + 3H_2S$.<br>The complete reaction is,<br>$Al_2(SO_4)_3 + 2(NH_4)_2S + 6H_2O = 2Al\ OH)_3 + 3H_2S + 3(NH_4)_2SO_4$. |

| *Experiment* | *Observations* | *Inference with explanation* |
|---|---|---|
| 4. Added $Na_2CO_3$ soln. | A white gelatinous ppt. is formed, which is soluble in excess of the reagent and also in dil. HCl. | The ppt. is of $Al(OH)_3$. Aluminium carbonate, which is initially formed, is completely hydrolysed to $Al(OH)_3$.<br>$Al_2(SO_4)_3 + 3Na_2CO_3 = Al_2(CO_3)_3 + 3Na_2SO_4$<br>$Al_2(CO_3)_3 + 6H_2O = 2Al(OH)_3 + 3H_2O + 3CO_2$.<br>$2Al(OH)_3 + Na_2CO_3 = 2NaAlO_2 + CO_2 + 3H_2O$ |

*It should be mentioned here, that the solution of sodium aluminate formed in the above reactions, gives the precipitate of $Al(OH)_3$ when boiled with $NH_4Cl$ (solution or solid).*

$$NaAlO_2 + NH_4Cl + H_2O = Al(OH)_3 \downarrow + NH_3 \uparrow + NaCl.$$

### Reactions of Zinc ion ($Zn^{++}$)

Used a solution of zinc sulphate, $ZnSO_4, 7H_2O$.

| *Experiment* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. Added NaOH soln. | A white gelatinous ppt. is formed. The ppt. is soluble in excess of the reagent and also in dil. HCl. | The white gelatinous ppt. is of zinc hydroxide which is soluble in excess of NaOH soln.. forming sodium zincate, $Na_2ZnO_2$, and also in dil. HCl, forming $ZnCl_2$.<br>$ZnSO_4 + 2NaOH = Zn(OH)_2 \downarrow + Na_2SO_4$.<br>$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$.<br>$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$. |

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 2. Added $NH_4OH$ soln. | A white gelatinous ppt. is formed. The ppt. is soluble in excess of ammonia and soln. of ammonium chloride (*distinction from aluminium*), and also in dil. HCl. | The ppt. is of zinc hydroxide which is soluble in excess ammonia and solutions of ammonium salts, forming complex compounds (soluble). It is also soluble in NaOH soln. and in dil. HCl due to the reactions shown above.<br>$ZnSO_4 + 2NH_4OH$<br>$Zn(OH)_2 \downarrow$<br>$+ (NH_4)_2SO_4$.<br>$Zn(OH)_2 + 6NH_4OH$<br>$= [Zn(NH_3)_6](OH)_2$<br>$+ 6H_2O$. |
| 3. Added ammonium sulphide soln. | A white ppt. is formed. The ppt. is insoluble in $NH_4OH$ and water, but soluble in mineral acids. | White zinc sulphide is precipitated. The ppt. is soluble in mineral acids, forming the corresponding zinc salts and producing $H_2S$.<br>$ZnSO_4 + (NH_4)_2S$<br>$= ZnS \downarrow$<br>$+ (NH_4)_2SO_4$.<br>$ZnS + 2HCl$<br>$= ZnCl_2 + H_2S \uparrow$. |

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 4 Added potassium ferrocyanide solution. | A white ppt. is formed. The ppt. is soluble in alkali, but insoluble in acetic acid. | The white ppt. is of zinc ferrocyanide, $Zn_2[Fe(CN)_6]$.<br>On adding excess of potassium ferrocyanide, a less soluble ppt. of zinc potassium ferrocyanide, $Zn_3K_2[Fe(CN)_6]_2$ is formed.<br>$2ZnSO_4 + K_4[Fe(CN)_6] = Zn_2[Fe(CN)_6]\downarrow + 2K_2SO_4$.<br>$3Zn_2[Fe(CN)_6] + K_4[Fe(CN)_6] = 2Zn_3K_2[Fe(CN)_6]_2$<br>Zinc ferrocyanide dissolves in NaOH soln., forming sodium zincate and sodium ferrocyanide.<br>$Zn_2[Fe(CN)_6] + 8NaOH = 2Na_2ZnO_2 + Na_4[Fe(CN)_6] + 4H_2O$. |
| 5. Added sodium phosphate soln., after adding $NH_4Cl$ soln. | A white ppt. is formed. The ppt. is insoluble in $NH_4OH$ and water, but soluble in mineral acids. | The white ppt. is of zinc ammonium phosphate, $Zn(NH)_4PO_4$. It dissolves in dil. acids, forming the corresponding zinc salts, and in excess of ammonia to form complex salt (soluble).<br>$ZnSO_4 + NH_4Cl + 2Na_2HPO_4 = Zn(NH_4)PO_4 + NaH_2PO_4 + Na_2SO_4 + NaCl$. |

### Reactions of Calcium ion ($Ca^{++}$)

Used a solution of calcium chloride, $CaCl_2, 6H_2O$.

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. Added $NH_4OH$ soln. | No precipitation. | — |
| 2. Added dil. $H_2SO_4$ to a concentrated soln. | A white ppt. is formed. The ppt. is soluble in hot ammoniumsulphate soln. ( *Distinction from barium and strontium.*) | White calcium sulphate is precipitated. (The ppt. is somewhat soluble in water). Ammonium sulphate forms a soluble complex salt with calcium sulphate.<br>$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl$.<br>$CaSO_4 + (NH_4)_2SO_4 = (NH_4)_2 [Ca(SO_4)_2]$. |
| 3. Added ammonium carbonate soln. in neutral or ammoniacal medium. | A white ppt. is formed. The ppt. is soluble in dil. HCl with the evolution of a gas. | White Calcium carbonate is precipitated. On treatment with dil. HCl, $CaCO_3$ decomposes into $CaCl_2$, $CO_2$ and water.<br>$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 \downarrow + 2NH_4Cl$.<br>$CaCO_3 + 2HCl = CaCl_2 + CO_2 \uparrow + H_2O$. |
| 4. Added ammonium oxalate soln. to a conc. solution of the sample, made ammoniacal with $NH_4OH$ soln. | A white crystalline ppt. is formed. The ppt. is insoluble in water, acetic acid or dil. $NH_4OH$, but readily dissolves in dil. HCl. | The white ppt. is of calcium oxalate.<br>$CaCl_2 + (NH_4)_2(COO)_2 = Ca(COO)_2 \downarrow + 2NH_4Cl$.<br>$Ca(COO)_2 + 2HCl = CaCl_2 + (COOH)_2$. |

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 5. Added potassium chromate soln. | No ppt. (*Distinction from barium and strontium.*) | Calcium chromat is fairly soluble in water. |
| 6. Added saturated calcium sulphate soln. | No ppt. (*Distinction from barium and strontium.*) | — |
| 7. Added di-sodium hydrogen phosphate soln. in ammoniacal medium. | A white ppt., soluble in dil. HCl, is formed. | Calcium phosphate is formed. This is soluble in dil. HCl.<br>$3CaCl_2 + 2Na_2HPO_4 + 2NH_4OH = Ca_3(PO_4)_2 + 4NaCl + 2NH_4Cl + 2H_2O$. |

**Reactions of Magnesium ion ($Mg^{++}$)**

Used a solution of magnesium sulphate, $MgSO_4, 7H_2O$.

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. Added NaOH soln. | A gelatinous white ppt. is formed. The ppt. is insoluble in excess of the reagent, but soluble in solutions of ammonium salts. | The gelatinous white ppt. is of magnesium hydroxide which is a fairly strong base and reacts with ammonium salts, liberating ammonia, the corresponding salt of the metal being formed.<br>$MgSO_4 + 2NaOH = Mg(OH)_2 \downarrow + Na_2SO_4$.<br>$Mg(OH)_2 + 2NH_4Cl = MgCl_2 + 2NH_4OH$. |

| *Experiments* | *Observations* | *Inference with explanation* |
|---|---|---|
| 2. Added ammonium hydroxide soln | A white gelatinous ppt. is formed, which is soluble in ammonium salts. | The ppt. is of $Mg(OH)_2$, whose behaviour towards ammonium salts has been stated earlier. |
| 3. Added ammonium carbonate soln. | A white ppt. is formed on boiling. If an ammonium salt is added before adding ammonium carbonate soln., no ppt. is obtained. | The white ppt. is of basic magnesium carbonate, $MgCO_3$, $Mg(OH)_2$, $5H_2O$. The non-formation of the ppt. in presence of ammonium salts is due to *common-ion effect*. [See Poddar & Haldar, *Higher Secondary Chemistry* §33]. |
| 4. Added $Na_2CO_3$ soln. | A voluminous white ppt. is formed. The ppt. is insoluble in bases, but soluble in acids and in solutions of ammonium salts. | The ppt. is of basic magnesium carbonate, which dissolves in acids, forming the corresponding magnesium salts.<br>$MgCO_3, Mg(OH)_2 + 4HCl = 2MgCl_2 + 3H_2O + CO_2$<br>The reason of solubility of the ppt. in ammonium salt solns. has been stated earlier. |

| *Experimets* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 5. Added di-sodium hydrogen phosphate soln. in presence of $NH_4OH$ and $NH_4Cl$ solns. | A white crystalline ppt. is formed. The precipitation is quickened by scratching the sides of the test tube with a glass rod. | The ppt. is of magnesium ammonium phosphate, $Mg(NH_4)PO_4$. As the salt has a tendency to form saturated solution cooling and scratching help to hasten its precipitation.<br>$MgSO_4 + Na_2HPO_4 + NH_4OH = Mg(NH_4)PO_4 + Na_2SO_4 + H_2O$.<br>The addition of $NH_4Cl$ during the reaction prevents the precipitation of $Mg(OH)_2$. |

## TESTS FOR ACID RADICALS

**I. Carbonate ($CO_3^=$).**

Used sodium carbonate, $Na_2CO_3, 10H_2O$.

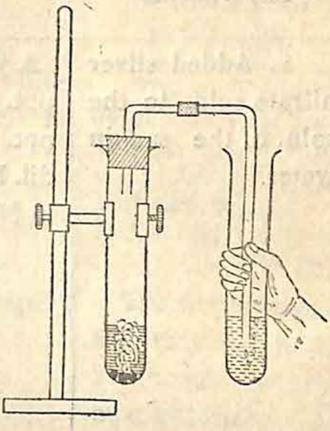
*Dry tests.—*

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. Taken a small quantity of the solid sample in a test tube and added 3-5 ml. of dil HCl to it. | An effervescence starts (i.e., a gas is evolved). The gas is colourless and odourless. | The gas may be $CO_2$ which is formed by the action of HCl on the carbonate,<br>$Na_2CO_3 + 2HCl = 2NaCl + CO_2\uparrow + H_2O$. |

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 2. The above experiment is carried out by taking the sample in a test tube fitted with a cork, through which a doubly bent delivery tube, as shown in the figure (p.145) passes. The open end of the delivery tube is dipped in another test tube containing clear and diluted lime-water. | The lime-water turns milky. | Lime-water is a solution of $Ca(OH)_2$ in water. On passing $CO_2$ through lime water, $CaCO_3$ (white) is formed, which being insoluble in water, remains suspended in the medium and imparts milkiness to the soln.<br>$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$. |
| 3. Passed the evolving gas through lime-water for sometime. (This may be done by adding some more sample and/or acid in the test tube where the gas is generated.) | The milkiness of lime-water disappears and a clear solution is again formed. But, the clear soln. becomes milky on boiling. | Calcium carbonate reacts with $CO_2$ in presence of water to form calcium bicarbonate, which is soluble in water.<br>$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$<br>Calcium bi-carbonate decomposes to give $CaCO_3$ on heating. |

[N.B. While carrying out the above experiments, it should be seen that no HCl passes through the delivery tube to the test-tube containing lime-water ; $CaCO_3$ is soluble in HCl ; so , presence of HCl in this test tube will not allow the formation of $CaCO_3$.]

A metallic sulphite also gives similar tests with lime-water. But, it is differentiated from a carbonate by the smell of the gas evolved ($SO_2$ has the smell of burning sulphur, while $CO_2$ has no smell) and also by the action of the evolved gas on acidified potassium dichromate soln. $SO_2$ turns the acidified potassium dichromate soln. green, but $CO_2$ has no action on this soln.



*Wet Test:* The wet test of the carbonate radical is feasible only with those carbonates which are soluble in water[e.g. $Na_2CO_3$; $K_2CO_3$, $(NH_4)_2CO_3$ etc.] As a carbonate decomposes on adding acid (such as HCl, $HNO_3$ or $H_2SO_4$) to it, with the evolution of $CO_2$ gas, the acid-solution of the salt does not contain carbonate radical and hence, no positive test by wet methods (as described below) can be expected. The following tests are, therefore, applicable to the water-soluble carbonates.

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. Added barium chloride (or calcium chloride) soln. to the soln. of the salt in water. | A white ppt. is formed. The ppt. dissolves in dilute mineral acids, but is insoluble in $NH_4OH$. | The white ppt. is due to barium carbonate ($BaCO_3$) [or calcium carbonate], which is insoluble in water, but soluble in mineral acids, with the evolution of $CO_2$, $Na_2CO_3 + BaCl_2 = BaCO_3 \downarrow + 2NaCl$, $(NH_4)_2CO_3 + CaCl_2 = CaCO_3 \downarrow + 2NH_4Cl$. $BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O$. $CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + CO_2 + H_2O$. $BaCO_3$ or $CaCO_3$ is not soluble in $NH_4OH$. |

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 2. Added silver nitrate soln. to the soln. of the salt in water. | A yellowish white ppt. is formed. The ppt. is soluble in dil. $HNO_3$ and also in $NH_4OH$. | The ppt. is of silver carbonate. It dissolves in $NH_4OH$ to form a complex salt (soluble). It is also decomposed by dil. $HNO_3$, giving a clear soln. and evolving $CO_2$.<br>$Na_2CO_3 + 2AgNO_3 = Ag_2CO_3 \downarrow + 2NaNO_3$<br>$Ag_2CO_3 + 2HNO_3 = 2AgNO_3 + CO_2 + H_2O$. |

It is, therefore, seen that the carbonate radical may be detected both by the dry and wet tests, if the sample is soluble in water. If the sample is not soluble in water, the carbonate radical is to be detected only by the dry tests.

**II. Chloride ($Cl^-$).**

Used sodium chloride, NaCl.

*Dry Tests.*—

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. A small quantity of the solid sample is taken in a test tube and 1 ml. of conc. $H_2SO_4$ is added to it. The mixture is then warmed over a Bunsen-flame. | A pungent smelling gas, with white fumes, is evolved. | May be chloride. Conc. $H_2SO_4$ reacts with a chloride, forming HCl gas which has a pungent smell, and the gas fumes in air.<br>$NaCl + H_2SO_4 = NaHSO_4 + HCl \uparrow$. |

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| (*a*) A glass rod moistened with $NH_4OH$ is held at the mouth of the test tube. | A dense white cloud (smoke) is formed. | The evolved gas is probably HCl, as it forms dense white cloud of $NH_4Cl$ with ammonia.<br>$HCl + NH_3 = NH_4Cl$. |
| (*b*) A moist blue litmus paper is held at the issuing gas. | The litmus paper turns red. | The gas is acidic and may be HCl. So, the sample may be a chloride. |
| 2. A small quantity of the sample is mixed with an equal amount of $MnO_2$ and the mixture is heated in a test tube with a few drops of conc. $H_2SO_4$. | A greenish yellow gas, with suffocating smell, is evolved. | The gas may be chlorine and the sample may be a chloride.<br>The chloride reacted with conc. $H_2SO_4$, forming HCl which was oxidised by $MnO_2$ to $Cl_2$.<br>$4HCl + MnO_2 = MnCl_2 + Cl_2 + 2H_2O$. |
| (*a*) A moist KI-starch paper is held in the greenish yellow gas. | The paper turns blue. | The evolving gas is chlorine and the sample is a chloride. Chlorine liberates iodine from potassium iodide, and this iodine has rendered starch-paper blue.<br>$2KI + Cl_2 = 2KCl + I_2$<br>Starch + $I_2$ → Blue colour. |

*Wet Tests* : Many metallic chlorides (except AgCl, $Hg_2Cl_2$) and $NH_4Cl$ are soluble in water. If the chloride is insoluble in water, it should be made soluble by treatment with some acid or by digesting with strong $Na_2CO_3$ soln. If digestion with $Na_2CO_3$ solution is resorted to, the extract should be filtered and the filtrate should be acidified with dilute nitric acid. But, in making solution of the salt in acid, HCl must not be used, as chloride ions will come from HCl, though the sample may not contain this radical. As the present syllabus includes only those samples which are soluble in dil HCl, these insoluble chlorides may not have to be dealt with by the students and hence, the relevant procedure is omitted. So, the sample should be soluble in water (hot or cold) and the following tests should be carried out with the aqueous solution.

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. To a small quantity of the soln. of the sample added silver nitrate soln. slowly.<br>The ppt. is divided into two parts : | A white curdy ppt. is formed. | The sample may be a chloride, as a chloride forms a curdy white ppt. of AgCl with $AgNO_3$ soln.<br>$NaCl + AgNO_3 = AgCl\downarrow + NaNO_3$. |
| (*a*) To one part of the ppt., added $NH_4OH$ (dil.). | The ppt. dissolves readily, giving a clear solution. | The ppt. may be of AgCl, as AgCl dissolves in $NH_4OH$, forming soluble silver ammine complex salt $AgCl + 2NH_4OH = [Ag(NH_3)_2]Cl + 2H_2O$. |
| To the clear soln obtained in (*a*), added dil. $HNO_3$. | The curdy white ppt. reappears. | Dil. $HNO_3$ decomposes the soluble silver ammine complex, forming AgCl again.<br>$[Ag(NH_3)_2]Cl + 2HNO_3 = AgCl + 2NH_4NO_3$. |

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| (*b*) To the other part of the ppt., added conc. $HNO_3$. | The ppt does not dissolve. | AgCl is insoluble in $HNO_3$. So, the ppt. is of AgCl and hence, the sample is a chloride. |
| 2. Added barium chloride soln. to the soln. of the sample. | No ppt. (*Difference from sulphate*) | — |
| 3. Added lead acetate soln. to the soln. of the sample. | A white ppt. is formed. The ppt. dissolves on heating, but re-appears on cooling. | The ppt. is probably of $PbCl_2$ which is soluble in hot water, but insoluble in the cold. Hence, the sample may be chloride. |

One characteristic test of chloride is the Chromyl Chloride Test. A small quantity of the solid sample is thoroughly mixed with three times its weight of powdered $K_2Cr_2O_7$, and equal amount of conc. $H_2SO_4$ is added to it. The mixture is then distilled by gently warming, when red vapours of chromyl chloride ($CrO_2Cl_2$) are formed. The vapours are absorbed in a soln. of NaOH, when a yellow soln. of sodium chromate ($Na_2CrO_4$) is formed. The soln. of sodium chromate is acidified with acetic acid and lead acetate soln. is added to it. Yellow ppt. of lead chromate is formed. The following sequence of reactions indicates that the original sample contained a chloride :

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 = 2CrO_2Cl_2 + 2KHSO_4 + 4NaHSO_4 + 3H_2O\ ;$$

$$CrO_2Cl_2 + 4NaOH = Na_2CrO_4 + 2NaCl + 2H_2O\ ,$$

$$Na_2CrO + Pb(CH_3COO)_2 = PbCrO_4 + 2CH_3COONa.$$

### * IIA. Bromide ($Br^-$).

Used sodium bromide, NaBr.

*Dry Tests.—*

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. Taken a small quantity of the solid sample in a test tube and added 2ml. conc. $H_2SO_4$. Warmed the mixture. | A reddish brown soln. is formed and reddish brown vapours are evolved, along with some other vapours fuming in moist air. | May be a bromide. Conc. $H_2SO_4$ reacts with a metallic bromide to produce HBr which is oxidised by conc. $H_2SO_4$ to $Br_2$. The reddish brown vapours are of bromine and the fuming vapours are due to undecomposed HBr gas.<br>$KBr + H_2SO_4 = KHSO_4 + HBr.$<br>$2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O.$ |
| 2. Mixed a little of the solid sample with equal quantity of $MnO_2$.<br>Added about 1 ml. of conc. $H_2SO_4$ to the mixture taken in a test tube and warmed. | Reddish brown vapours, with irritating smell, are evolved. | The vapours are of $Br_2$, which is formed by the action of $MnO_2$ and conc. $H_2SO_4$ on bromide : $2KBr + MnO_2 + 3H_2SO_4 = Br_2 + 2KHSO_4 + MnSO_4 + 2H_2O.$ |
| Held a strip of filter paper soaked in starch soln. in the vapour. | The paper turns orange-red in colour. | The vapour is of $Br_2$. Hence, the salt is a bormide. |

*Wet Tests ;*

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. Taken a soln. of the sample in water and added $AgNO_3$ soln. to it. | A curdy, pale-yellow ppt. is formed. The ppt. is insoluble in $HNO_3$, sparingly soluble in dil. $NH_4OH$, but readily soluble in conc. $NH_4OH$. | The pale yellow ppt. is of AgBr, which has the observed solubility characteritsics.<br>$KBr + AgNO_3 = AgBr + KNO_3$.<br>$AgBr + 2NH_3 = [Ag(NH_3)_2]Br$.<br>(soluble complex.) |
| 2. Added about 1 ml. of chlorine-water to a soln. of the sample in water. Then added 3-4 ml. of chloroform (or $CS_2$ or $CCl_4$) to the mixture, shaken and allowed to stand. | The lower chloroform layer is coloured orange-red. | The sample is a bromide. Chlorine-water liberates bromine from the bromide and the liberated bromine dissolves in $CHCl_3$, making its colour orange-red.<br>$2KBr + Cl_2 = 2KCl + Br_2$. |

*** II B. Iodide ($I^-$).**

Used potassium iodide, KI.

*Dry Tests.—*

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. Taken a small quantity of the solid sample in a test tube. Added 1-2ml. of conc. $H_2SO_4$ and warmed. | Violet vapours are evolved, which turn a starch-paper blue. | The violet vapours are of iodine and the sample may be an iodide Conc. $H_2SO_4$ reacts with an iodide, producing HI, which is immediately oxidised by conc. $H_2SO_4$ to $I_2$. The liberated iodine turns the starch paper blue.<br>$KI + H_2SO_4 = KHSO_4 + HI$.<br>$2HI + H_2SO_4 = I_2 + SO_2 + 2H_2O$. |

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 2. Warmed a mixture of the sample and $MnO_2$ with conc. $H_2SO_4$. | Violet vapours, as in the above experiment, are evolved | Same inference as above. The following reaction takes place in this case : $2KI + MnO_2 + 3H_2SO_4 = I_2 + 2KHSO_4 + MnSO_4 + 2H_2O$. |

*Wet Tests :*

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. Added $AgNO_3$ soln. to an aqueous soln. of the sample. | A curdy yellow ppt. is formed. The ppt. is insoluble in $HNO_3$, sparingly soluble even in conc. $NH_4OH$, but readily soluble in sodium thiosulphate soln. | The ppt. is of AgI and the sample may be an iodide. AgI has the observed solubility characteristics. It dissolves in sodium thiosulphate soln., forming a soluble complex salt.<br>$KI + AgNO_3 = AgI \downarrow + KNO_3$ |
| 2. Added a little chlorine-water to the aqueous soln. of the sample taken in a test tube, and shaken with chloroform. Allowed the mixture to settle. (Avoided excess of chlorine-water'. | A violet colour of the lower layer of chloroform is formed. | Chlorine-water liberates iodine from the iodide and iodine dissolves in chloroform to give a violet colour. |

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 3. Added a soln. of mercuric chloride to the aqueous soln. of the sample. | A scarlet ppt., is formed, which dissolves into a colourless soln. on adding excess of the sample soln. | The salt may be an iodide Mercuric chloride reacts with an iodide to form $HgI_2$ (scarlet), which dissolves in excess of the iodide to form colourless $K_2[HgI_4]$ (soluble in water).<br>$2\ KI + HgCl_2 = 2\ KCl + HgI_2$.<br>$HgI_2 + 2\ KI = K_2[HgI_4]$. |
| 4. Added sodium nitrite soln. to the aqueous soln. of the sample acidified with dil. acetic acid (or dil. $H_2SO_4$). Added starch soln. to the mixture. | A deep blue colour is formed. | The salt may be an iodide. $HNO_2$ and HI are liberated by the action of the acid on $NaNO_2$ and KI respectively. $HNO_2$ and HI interact to produce iodine which forms blue colour with starch.<br>$2HNO_2 + 2HI = I_2 + 2NO + 2H_2O$. |

**III. Nitrate ($NO^-_3$).**

Used Potassium Nitrate, $KNO_3$.

*Dry Tests.—*

**Action of heat :** When a solid sample of a nitrate is strongly heated in a test tube, the results observed vary with the metal associated with the nitrate radical. For example, sodium and potassium nitrates decompose into the corresponding nitrites, with the evolution of oxygen (which can be tested by a glowing chip of wood which is re-kindled by the evolved gas). Ammonium nitrate decomposes into $N_2O$ and $H_2O$. Nitrates of other heavy metals like Ag, Pb etc. decompose into $O_2$ and $NO_2$ (evolution of brown fumes) :

$2KNO_3 = 2KNO_2 + O_2 \uparrow$ ; $NH_4NO_3 = N_2O + 2H_2O$ ;
$2AgNO_3 = 2Ag + 2NO_2 \uparrow + O_2 \uparrow$ ;
$2Pb(NO_3)_2 = 2PbO + 4NO_2 \uparrow + O_2 \uparrow$ .

The other-tests of nitrate are as follows :

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. Taken a small quantity of the solid sample in a test tube and heated it with a few drops of conc. $H_2SO_4$. | Reddish brown fumes, along with pungent acid vapours (which fume in air) are evolved. | The reddish brown fumes are of $NO_2$ and the acid vapours are of $HNO_3$. These are formed by the action of conc. $H_2SO_4$ on a nitrate and subsequent heating. Hence, the salt may be a nitrate.<br>$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$<br>$4HNO_3 = 4NO_2 + O_2 + 2H_2O$. |
| 2. Heated a little of the solid sample with a few drops of conc. $H_2SO_4$ and some pieces of bright copper turnings. | Reddish brown fumes are evolved and a blue soln. is obtained. | The brown fumes are of $NO_2$. Conc. $H_2SO_4$ liberates $HNO_3$ from the metal nitrate. The liberated $HNO_3$ reacts with the copper turnings, forming $NO_2$ gas and copper nitrate in soln., which is blue in colour.<br>$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$. |

*Wet tests* : All nitrates are more or less soluble in water. So, an aqueous soln. of the salt shall be used.

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| **1. The Ring Test :** Added about 3 ml. of a freshly prepared soln. of $FeSO_4$ to 3ml. of the soln. of the sample and mixed well. Now, carefully added, along the side of the test tube (without much disturbing the soln.), about 5 ml. of conc. $H_2SO_4$, so that the added acid forms a layer beneath the mixture. | A brown ring is formed at the junction of the two liquid layers. | The brown ring is due to $FeSO_4.NO$, which is formed by the following reactions :<br>$NaNO_3+H_2SO_4 = NaHSO_4+HNO_3$.<br>$6\,FeSO_4+2HNO_3+3H_2SO_4 = 3Fe_2(SO_4)_3+2NO+4H_2O$ ;<br>$FeSO_4+NO = FeSO_4.NO$(*brown*).<br>*The borwn ring disappears on shaking or warming, when NO evolves as a gas and yellow solution of the ferric sulphate remains.*<br>If the test is not carried out carefully, sometimes, the whole soln. becomes brown, instead of the formation of a ring. |
| 2. Taken 2-3 ml. of the soln. of the sample in a test tube and added some zinc powder (or *Devarda's alloy*) and about 5 ml. of strong NaOH soln. Warmed the mixture.<br>(Aluminium may also be used in place of zinc.) | $NH_3$ is evolved, as detected by the smell of the gas and its action on red litmus paper (turns blue), or by the production of dense white fumes with a glass rod moistened with conc. HCl. | $NH_3$ is formed by the reduction of nitrate by nascent hydrogen obtained by the reaction of NaOH on zinc (or Devarda's alloy). $NH_3$ gives the observed reactions.<br>$NaNO_3+4Zn+7NaOH = NH_3+4Na_2ZnO_2+2H_2O$. |

***III A : Nitrite ($NO^-_2$).**
Used Sodium Nitrite, $NaNO_2$.
*Dry tests.*—

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| **1.** Taken a little of the solid sample in a test tube and added 5ml. dil. HCl. Warmed the mixture. | Brown fumes are evolved. | The brown fumes are of $NO_2$. Dil. HCl liberates unstable $HNO_2$ from a nitrite. On warming, $HNO_2$ decomposes into $HNO_3$, NO and $H_2O$. Nitric oxide combines with oxygen of air to form brown $NO_2$. Hence, the sample may be a nitrite.<br>$NaNO_2 + HCl = HNO_2 + NaCl$ ;<br>$3HNO_2 = HNO_3 + 2NO + H_2O$ ;<br>$2NO + O_2 = 2NO_2$. |

*Wet Tests.* – Except silver nitrite, all other nitrites are freely soluble in water. So, an aqueous solution of the sample may be used.

| *Experiments* | *Observations* | *Inference with Explanation* |
|---|---|---|
| 1. **Ring Test :** Carried out the test as described for *nitrate*, but using dil. acetic acid or dil. $H_2SO_4$ (instead of conc. $H_2SO_4$). | A brown ring is formed or a brown colour of the soln. results.<br>(*Distinction from nitrate which responds to this test only when conc. $H_2SO_4$ is added.*) | The brown ring or colour is due to $FeSO_4.NO$. Dil. $H_2SO_4$ or dil. acetic acid is capable of liberating $HNO_2$ from a nitrite. $HNO_2$ breaks up to give NO, which forms $FeSO_4.NO$.<br>$2NaNO_2 + 2CH_3.COOH = 2HNO_2 + 2CH_3COONa$ ;<br>$3HNO_2 = H_2O + HNO_3 + NO$ ;<br>$FeSO_4 + NO = FeSO_4.NO$. |

| *Experiments* | *Observations* | *Inferences with Explanation* |
|---|---|---|
| 2. Warmed a small quantity of the soln. of the sample with excess of solid $NH_4Cl$. | A gas is evolved. | The gas is $N_2$, which is formed according to the equation,<br>$NaNO_2 + NH_4Cl$<br>$= NaCl + N_2 \uparrow$<br>$+ 2H_2O$. |
| 3. Added 1-2 ml. of KI. soln. to the soln. of the sample (3ml.), and acidified the mixture with dil. acetic acid or dil. $H_2SO_4$. | The soln. turns brown. It becomes deep blue when starch soln. is added to it. | The brown colour of the soln. is due to iodine which turns blue by starch soln. Iodine is liberated during the expt. by the following reactions :<br>$NaNO_2 + CH_3COOH$<br>$= HNO_2$<br>$+ CH_3COONa$.<br>$2KI + 2HNO_2$<br>$+ 2CH_3COOH$<br>$= 2CH_3COOK + I_2$<br>$+ 2NO + 2H_2O$. |

**A very sensitive test for nitrite is carried out as follows :**

1 ml. of the soln. of the sample is mixed with 1 ml. of sulphanilic acid reagent, followed by the addition of 1 ml. of α-naphthylamine reagent. A beautiful red colour or ppt. is obtained. The colour is due to the *diazotization* of sulphanilic acid by the nitrite, followed by *coupling* of the *diazo-salt* with α-naphthylamine, when the red *dye* is formed. [See Poddar & Haldar, Higher Secondary Chemistry, §46 (Aromatic amines)].

### IV. Sulphide ($S^{=}$).

Used Sodium sulphide, $Na_2S, 9H_2O$.

*Dry Tests.*

| *Experiments* | *Observations* | *Inferences with Explanation* |
|---|---|---|
| 1. Taken a small quantity of the solid sample in a test tube. Added 2-3 ml. of dil. HCl or dil. $H_2SO_4$ and heated. | A gas, with smell of rotten eggs, is evolved. | The gas may be $H_2S$ with that characteristic smell and hence, the sample may be a sulphide.<br>$Na_2S + 2HCl = 2NaCl + H_2S\uparrow$. |
| Held a piece of filter paper moistened with lead acetate soln. or silver nitrate soln. in the evolved gas. | The filter paper turns black. | The gas is $H_2S$, as it reacts with lead acetate and silver nitrate solns. to give black PbS or $Ag_2S$.<br>$Pb(CH_3COO)_2 + H_2S = PbS + 2CH_3COOH$.<br>$2AgNO_3 + H_2S = Ag_2S + 2HNO_3$. |
| Held a piece of bright Ag foil in the evolved gas. | The Ag foil turns black. | Black $Ag_2S$ is formed. |

*Wet Tests* : Except the alkali metal sulphides and ammonium sulphide, all other metallic sulphides are more or less insoluble in water. In making solutions in dil. HCl, the sulphides decompose with the liberation of $H_2S$ gas. Hence, the resultant solutions hardly contain sulphide ions. For sulphides insoluble in water, only the dry tests (as stated above) should be performed. The wet tests (given below) are to be carried out with an aqueous solution of a soluble sulphide, (*e.g.* $Na_2S, 9H_2O$).

| *Experiments* | *Observations* | *Inferences with Explanation* |
|---|---|---|
| 1. Added $AgNO_3$ soln. to a soln. of the sample. | A black ppt., soluble in hot dil. $HNO_3$, is formed. | The black ppt. is of $Ag_2S$, which is insoluble is cold, dil. $HNO_3$, but soluble in the hot. $Na_2S + 2AgNO_3 = Ag_2S + 2NaNO_3$. |
| 2. Added lead acetate soln. to the soln. of the sample. | A black ppt, is formed, which is soluble in dil. $HNO_3$. | The black ppt. is of PbS. It is soluble in dil. $HNO_3$. |
| 3. Added $BaCl_2$ soln to the soln. of the sample. | No ppt. | — |
| 4. Added 2-3 drops of sodium nitroprusside soln. to the soln. of the sample. | A violet colour is formed. | The violet coloration is due to the formation of a complex salt, $Na_2S + Na_2[Fe(CN)_5NO] = Na_4[Fe(CN)_5NOS]$. (violet) |

**V. Sulphate ($SO_4^{=}$).**

Used Sodium Sulphate, $Na_2SO_4, 10H_2O$.

*Dry Tests,*—There is no *direct* dry test for a sulphate ion. The following two tests may, however, be done :

| *Experiments* | *Observations* | *Inferences with Explanation* |
|---|---|---|
| 1. Taken a small quantity of the solid sample in a test tube and heated it first with dil. $H_2SO_4$ and then with conc. $H_2SO_4$. | No gas or vapour is evolved. | The only inference that can be drawn from this test is that the sample does not contain $CO_3^{=}$, $S^{=}$, $Cl^-$, ($Br^-$, $I^-$) or $NO_3^-$,($NO_2^-$) ions. |

| *Experiments* | *Observations* | *Inferences with Explanation* |
|---|---|---|
| 2. Mixed a small quantity of the sample with 3 times its bulk of anhydrous $Na_2CO_3$ and heated the mixture for some time in a cavity of a charcoal block under reducing flame. [See *Charcoal Block Test.*] The mass is then cooled, transferred in a test tube and treated with dil. HCl. | A gas with bad smell, like that of rotten eggs, is evolved. The gas turns a lead acetate paper black. | The evolved gas is $H_2S$ The sulphate in the sample has been reduced to a sulphide by the charcoal-block reduction. The resultant sulphide liberates $H_2S$ on reaction with dil. HCl.<br>$Na_2SO_4+4C = Na_2S+4CO$ ;<br>$Na_2S+2HCl = H_2S\uparrow+2NaCl$. |

*Wet Tests.*—Sulphates of Ba, Sr and Pb are insoluble in water, while $CaSO_4$ and $HgSO_4$ are slightly soluble in water. Sulphates of other metals are generally soluble in water. Wet tests for the sulphate radical may be done with aqueous solns. or with solutions in dil. HCl.

| *Experiments* | *Observations* | *Inferences with Explanation* |
|---|---|---|
| 1. To a small quantity of the soln. of the sample, added barium chloride (or barium nitrate) soln. [The aqueous sample soln. should be acidified with dil. HCl. | A granular white ppt. is formed. The ppt. is insoluble in conc. HCl or conc. $HNO_3$. | The ppt. is of barium sulphate. $BaSO_4$ is insoluble in conc. HCl or conc. $HNO_3$.<br>$CuSO_4+BaCl_2 = BaSO_4\downarrow+CuCl_2$.<br>$Al_2(SO_4)_3+3BaCl_2 = 3BaSO_4\downarrow+2AlCl_3$, [Sulphites ($SO_3^=$) and carbonates ($CO_3^=$) in neutral solns. form white ppt. with $BaCl_2$, but these ppts. are soluble in HCl or $HNO_3$.] |

| *Experiments* | *Observations* | *Inferences with Explanation* |
|---|---|---|
| 2. Added $AgNO_3$ soln. to a dil. aqueous soln.of the sample. | No ppt. | The quantity of $Ag_2SO_4$ formed remains in soln.due to its solubility.<br>[N.B. Do not add $AgNO_3$ soln. to a soln. of the sample which is acidified with HCl. In such cases, AgCl will be precipitated ] |

**Systematic Preliminary Tests For Acid Radicals.**

As prescribed in the syllabus, only *one* acid radical in a single unknown salt is to be detected. Instead of carrying out tests for individual acid radicals from the very beginning of the analysis, it would be easier and less time-consuming to follow the systematic procedure outlined below with the unknown sample to get some preliminary ideas about the radical present, and then to cofirm it by the tests of that individual ion as given earlier.

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| **Dry Tests :** | | |
| i. To a small quantity of the sample taken in a test tube, added dil. HCl(or dil. $H_2SO_4$); observed the effect in the cold or on warming. | (*a*) A colourless and odourless gas is evolved with effervescence. The gas turns lime-water milky. | May be carbonate. |
| | (*b*) A colourless gas, with smell of rotten eggs, and turning a lead-acetate paper black is evolved. | May be sulphide. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 2. To a small quantity of the sample taken in a test tube, added 2-3 ml. of conc. $H_2SO_4$ and warmed. | (*a*) Brisk evolution of a gas like the one in expt. I *a*). | May be carbonate. |
| | (*b*) Brisk evolution of a gas like the one in expt. I(*b*). | May be sulphide. |
| | (*c*) A brown gas is evolved. | May be nitrate, nitrite (or bromide). |
| | (*d*) Violet vapours are formed. | May be iodide. |
| | (*e*) A pungent-smelling, colourless gas is evolved. The gas fumes in air. | May be chloride, bromide or nitrate. |
| (i) A moist blue litmus paper is held in the evolved gas. | The litmus paper turns red. | May be chloride, bromide or nitrate. |
| (ii) A glass rod moistened with ammonia is held in the gas. | Dense white fumes are formed. | May be chloride, bromide or nitrate. |
| 3. A small quantity of the sample is mixed with $MnO_2$ in a test tube, conc. $H_2SO_4$ is added and the mixture is heated. | (*a*) A greenish yellow gas, with pungent smell (like bleaching powder) is evolved. The gas turns starch-iodide paper blue. | Most probably a chloride. |
| | (*b*) A reddish brown vapour is evloved. The vapour turns starch-iodide paper blue. | May be bromide. |
| | (*c*) A violet vapour is evolved which turns a starch-paper blue. | May be an iodide. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 4. A small quantity of the sample is heated with conc. $H_2SO_4$ after adding some pieces of copper turnings. | Deep brown fumes are formed. | May be nitrate (or nitrite). |
| **Wet Tests.—** | | |
| 1 To a soln. of the sample in water, added $AgNO_3$ soln. | (*a*) A curdy white ppt. is formed. The ppt. is insoluble in $HNO_3$, but *completely* soluble in $NH_4OH$ soln. | Chloride. |
| | (*b* A light yellow curdy ppt. is formed. The ppt. is insoluble in $HNO_3$, but dissolves in strong $NH_4OH$ with difficulty. | Bromide. |
| | (*c*) A yellow curdy ppt. is formed. The ppt. is insoluble in $NH_4OH$ and $HNO_3$. | Iodide. |
| | (*d*) A white ppt. is formed, but the ppt. is soluble in dil. HCl or dil. $HNO_3$ with the evolution of a gas ($CO_2$). The ppt. is also soluble in $NH_4OH$. | May be a carbonate. |
| 2. To an aqueous soln of the salt (or solution in dil. HCl), is added $BaCl_2$ or $Ba(NO_3)_2$ soln. | A heavy white crystalline ppt. is formed. The ppt is insoluble in mineral acids and in $NH_4OH$ | Sulphate. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 3. Performed **Ring Test** with the aqueous soln. (with conc. $H_2SO_4$). | A brown ring is formed. | Nitrate (**or nitrite**). |
| Repeated the test with dil. $H_2SO_4$ or acetic acid. | A brown ring is formed. | Nitrite. |
| 4. To an aqueous soln. of the sample added 2-3 drops of sodium nitroprusside soln. | A violet colour is formed. | Sulphide. |

### Systematic Wet Tests For Basic Radicals

In the West Bengal Syllabus, two basic radicals are to be identified in a mixture (out of eight radicals, *viz*. $Pb^{++}$, $Cu^{++}$, $Fe^{++}$, $Fe^{+++}$, $Al^{+++}$, $Zn^{++}$, $Ca^{++}$ and $Mg^{++}$). The unknown sample should be soluble in water or dil. HCl The mixture may contain acid radical(s), but it need not be detected in the particular sample. It may be possible to identify both the unknown basic radicals by the individual tests of these ions, but it is advisable and customary to resort to the *Group Analysis* of the sample.

In the Group Analysis of the basic radicals, all the cations* are divided into five groups (I—V), the groups II and III being divided into sub-group A and sub-group B each. The basic radicals are precipitated in one or the other group of this classification on treatment with some *reagents* which are called the *group reagents.* These are (i) dil. HCl for Group I, (ii) $H_2S$ in acid medium for Group II, (iii) solid $NH_4Cl$ and $NH_4OH$ soln. for Group IIIA, (iv) $H_2S$ in ammoniacal medium for Group IIIB, (v) $(NH_4)_2CO_3$ in ammoniacal medium for Group IV and (vi) $Na_2HPO_4$ soln. in ammoniacal medium for Group V (for Mg). The cations included in the groups are :

Group I—[$Ag^+$, $Hg_2^{++}$]*, $Pb^{++}$ ;
Group IIA—[$Hg^{++}$],*$Pb^{++}$, $Cu^{++}$, [$Bi^{+++}$, $Cd^{++}$]* ;

---

*Ions shown in parentheses are not included in W. B. Syllabus.

Group II B— [$As^{+++}$, $Sb^{+++}$, $Sn^{++}$]* ;
Group III A— $Fe^{++}$, $Fe^{+++}$, $Al^{+++}$; [$Cr^{+++}$, $Mn^{++}$]* ;
Group III B— $Zn^{++}$ ;
Group IV—[$Ba^{++}$, $Sr^{++}$]*, $Ca^{++}$ ;
Group V—$Mg^{++}$.

The precipitation of these metal ions in a particular group is due to the (i) insolubility of the chlorides of group I metals in dil. HCl, (ii) insolubility of the sulphides of group II metals in dil. HCl, (ii) insolubility of the hydroxides of group III A metals in ammoniacal medium, (iv) insolubility of the sulphide of group IIIB metal (Zn) in ammoniacal medium, (v) insolubility of the carbonates of group IV metals in ammoniacal medium and (vi) insolubility of $MgNH_4PO_4$ in ammoniacal medium. Sodium and potassium have no particular group reagent, but they are identified by the individual tests.

**N.B.** It is desirable that the students should be acquainted and conversant with the group analysis of metal ions, as this will be of profound help to them in future.

The **first step** in performing the group analysis of the metal ions by systematic wet tests is to prepare a solution of the given solid sample. As the present syllabus prescribes samples soluble in water or dil. HCl, it is suggested that the student should prepare the solution in the following way :

*Preparation of solution* : About 0·2-0·5 gms. of the finely powdered solid sample are taken in a clean beaker (100 ml. capacity), and 25-30 ml. of distilled water are added to it. The mixture should be stirred with a clean glass rod. If the sample almost completely dissolves (some haziness may exist in certain cases), the solution is filtered in another beaker and the filtrate is used for analysis. If the sample does not dissolve or is partly dissolved, heat the beaker gently on a burner, with occasional stirring, to effect dissolution. The hot solution may be filtered if there be slight turbidity. It should be pointed out here that many inorganic salts (like $PbCl_2$) are soluble in hot water but the solid salt crystallises out on cooling the solution. In such cases, a smaller quantity of the sample should be disssolved in a larger volume of water and experiments should be performed with warm solutions. If the sample is not soluble even in hot water, the supernatant clear liquid from the beaker may be decanted (the insoluble residue should not be thrown away during decantation) and the wet sample should be treated with dil. HCl (25-30 ml.), and solution of the sample should be made as described with water (at first at ordinary temperature and, if still partly insoluble, then by heating). The solution, thus made, is the '*stock solution*' of the sample and it should be kept carefully. Not more than 2 ml. of this solution should be used for each individual test and about 20 ml. for the Group Analysis.

It should be mentioned that the student should keep eyes and nose open during effecting the solution of the solid sample, because many indications regarding the nature of the sample are obtained during this process. For example, while preparing the solution in dil. HCl, carbonates and sulphides will evolve gases ($CO_2$ and $H_2S$ respectively). Solubility characteristics (i. e. solubility in water, hot or cold, and in dil. HCl) of the solid salt may also indicate the nature of the sample (*e.g.* if the sample is soluble in hot water but is precipitated on cooling the solution, lead chloride *may* be present).

Although individual tests for the basic radicals may be done with the solution of the sample obtained above, we would give here the systematic procedure of **Group Analysis** with the solution. One essential point is to be noted at the very outset of the group analysis of the matals which, if neglected, will invariably cause trouble in such analysis :

*While separating the metal(s) occuring in a particular group by the relevant reagent and procedure, be sure that the whole of the particular metal(s) is precipitated and nothing of it is left in solution ; otherwise, this will invariably be precipitated in subsequent groups and lead to wrong inferences.*

In the group analysis of a mixture of the basic radicals, the metals are first separated into different groups by the formation of precipitates with the appropriate group reagents. The precipitate of each group is then further analysed to find out their contents and make the correct inference regarding any particular metal ion by performing its *confirmatory test(s)*.

In performing the Group analysis, we add the *group regent* to the solution to find out whether the metallic ions (basic radicals) occuring in the particular group are present or not. If a precipitate is formed, it is indicated that one or more of the basic radicals of that group may be present. If no precipitate is formed, we may infer that metal(s) of that group is not present in the solution. If a ppt. is formed, it is filtered and the test for the next group is performed with the filtrate.

The routine procedure for Group analysis is given below. As only eight radicals ($Pb^{++}$, $Cu^{++}$, $Fe^{++}$, $Fe^{+++}$, $Al^{+++}$, $Zn^{++}$, $Ca^{++}$ and $Mg^{++}$) are included in **West Bengal Syllabus**, a simplified procedure is given here. Group analysis with large number of basic radicals (as included in **Gauhati Syllabus**) will be given in a separate **Appendix.**

1. **Group I.** Radicals in this group should be tested in aqueous solution. If the sample is completely soluble in dil. HCl (even in the cold), it may be safely inferred that the basic radical included in this group, viz. $Pb^{++}$, is not present, as $PbCl_2$ is sparingly soluble in cold dil. HCl, and a ppt, of it would be formed when the soln. dil. HCl is cooled down. If the sample is soluble in water, dil. HCl should be added to it. If a ppt. is formed (*white*), then $Pb^{++}$ is present. The ppt. is filtered and preserved for *confirmatory test* of $Pb^{++}$ ions. The filtrate is subjected to tests for Group II metal ions.

2. **Group II.** Take about 2 ml. of the filtrate (from 1) in a test tube and add 2 ml. of distilled water. Warm and pass $H_2S$ gas from the Kipp's apparatus (Use your own glass tube for passing the gas). If a ppt. is formed,* the whole of the above filtrate should be taken ·for the experiment. This is diluted, warmed and $H_2S$ is passed till no more precipitation occurs. (This may be tested by filtering off a small portion of the mixture containing the ppt. and passing $H_2S$ into the filtrate). The ppt. (*black*) is filtered and the residue may contain $Cu^{++}$ and/or $Pb^{++}$ ions, whose sulphides are insoluble in dil. HCl. The filtrate is used for the analysis of of the next group. Preserve the ppt. for confirmatory tests.

---

*If no ppt. is formed by $H_2S$ in the 2 ml.-test solution, it is evident that Group II metals are not present in the soln. and it is, therefore, not necessary to pass $H_2S$ through the bulk of the filtrate. The test solution is discarded and we proceed the next group (Group IIIA) with the rest of the filtrate.

It may be noted that $Pb^{++}$ is precipitated as $PbCl_2$ in group I and also as PbS (black) in group II. This is due to the fact that $PbCl_2$ is somewhat soluble in dil. HCl and this dissolved $PbCl_2$ is precipitated in Group II as PbS (*black*).

(3) **Group IIIA.** If a ppt. is formed in Group II (*i.e.,* if $H_2S$ gas was passed through the whole soln.), the filtrate obtained is boiled on a wire-gauge over a Bunsen burner till $H_2S$ is completely expelled from the soln. ( This may be tested by the odour of the evolving vapours, or by holding a piece of filter paper moistened with lead acetate soln. in the vapour. If the filter paper is not *blackened*, then $H_2S$ is completely driven off from the soln.). The soln.. freed from $H_2S$, is diluted with a little quantity of distilled water, if necessary, and 3-5 drops of conc. $HNO_3$ is added to it and warmed. [ This oxidises any ferrous salt which was formed by the reduction by $H_2S$ of a ferric salt which might have been present in the sample.] About 1 gm. of solid ammonium chloride is added to the soln., followed by the addition of an excess of ammonium hydroxide soln., till the test soln. is definitely ammoniacal. Heat the soln. A ppt. (*white or brown*) is formed, if metal ions of this Group (*viz.* $Fe^{++}$, $Fe^{+++}$ or $Al^{+++}$) are present. Filter the ppt. and preserve it for *confirmatory tests* and proceed to the next group with the filtrate.

N.B. (*a*) The ppt. formed in this group is of the hydroxides of $Fe^{+++}$ and $Al^{+++}$ ions, which are insoluble in ammonia in presence of $NH_4Cl$. It should be remembered that any ferrous salt that might have been present in the sample is oxidised to ferric salt by the treatment made. So, if ferric hydroxide ppt. is obtained, it cannot be definitely inferred whether the sample contained the ferrous or the ferric salt (or both). In such cases, it is advisable to carry out the differntiating tests (see page 135) with the original smaple. It may also be pointed out that ferrous salts, being very susceptible to aerial oxidatian, may be partly oxidised during storage, and even if a ferrous salt is present in the unknown sample, some positive tests of ferric ions may be given by the sample. The student is to judge the relative amounts of the two ions present from the results of his tests. If the tests indicate minute amount of ferric ion, it may be taken to be due to the aerial oxidation of the given ferrous salt.

(*b*) If the sample does not contain metal ions of Group II as indicated by the test-solution in (2), and consequently no $H_2S$ gas was passed into the filtrate from Group I, the treatment with conc. $HNO_3$ may be avoided. In such cases, if a ferrous salt is present in the sample, a *dirty green* gelatinous ppt. (turning brown on exposure to air) will be obtained.

(4) **Group III B.** Through the filtrate from Group III A, pass $H_2S$, till no more ppt. is formed. A *white* ppt. is obtained if zinc is present. Zinc sulphide is precipitated, as it is insoluble in ammoniacal medium Filter the ppt. and preserve it for *confirmatory tests.* Proceed with the filtrate for testing the Group IV radicals.

(5) **Group IV.** The filtrate from Group III B is taken in a small beaker and boiled gently on a burner till $H_2S$ is completely expelled. (This may be tested with a lead acetate-paper as stated earlier.) The filtrate may be too small in volume and as such, it should be diluted with a little distilled water and made ammoniacal with $NH_4OH$ soln. A concentrated soln. of ammonium carbonate is then added to it. A white ppt. is obtained if calcium is present. The ppt. is of $CaCO_3$ which is insoluble in ammoniacal soln. The ppt. is filtered, the residue is preserved for *confirmatory tests*, and test for the next Group (Group V) radical is carried out with the filtrate.

(6) **Group V.** The filtrate is concentrated to about 10—15 ml. in volume and disodium hydrogen phosphate soln. is added to it. The test soln. should be ammoniacal. If necessary, the walls of the beaker may be scratched with a glass rod. A white ppt. of $Mg(NH_4)PO_4$ is formed if magnesium is present. The ppt. should be retained for the *confirmatory tests* and the filtrate may be rejected.

It is desired and conventional to present the above experiments and observations in a *tabular form* as shown below :

## Group Analysis for Metal Ions (Basic Radicals)

To a soln.* of the sample, added a few drops of dil. HCl in the cold. If a ppt. is formed, added more dil. HCl until no further precipitation takes place. Filtered.

<table>
<tr><td rowspan="5">A white ppt. is formed. $Pb^{++}$ present. (Group I)</td><td colspan="5">Filtrate : Heated nearly to boiling and passed $H_2S$ till saturated. Filtered.</td></tr>
<tr><td rowspan="4">A Black ppt. is fromed. $Cu^{++}$ and/or $Pb^{++}$ may be present. (Group II)</td><td colspan="4">Filtrate : Boiled until $H_2S$ is completely removed. Added 1 – 2 ml. conc. $HNO_3$. Boiled for one minute, cooled and added 1 – 2 gms. of solid $NH_4Cl$ and again heated to boiling. Now added excess of $NH_4OH$ soln. A gelatinous ppt. may be formed. Filtered.</td></tr>
<tr><td rowspan="3">A brown or white gelatinous ppt. is formed. $Fe^{+++}$ (also $Fe^{++}$) and/or $Al^{+++}$ may be present (Group III A).</td><td colspan="3">Filtrate : Warmed and passed $H_2S$ gas (till no more ppt. is formed). Filtered.</td></tr>
<tr><td rowspan="2">A white ppt. is formed. $Zn^{++}$ present (Group III B.)</td><td colspan="2">Filtrate : Boiled off $H_2S$. Added a little solid $NH_4Cl$ and $NH_4OH$ soln. Then added a conc. soln. of $(NH_4)_2CO_3$ (preferably dissolved in dil. $NH_4OH$ soln.) and warmed. Filtered.</td></tr>
<tr><td>A white ppt. is fromed. $Ca^{++}$ present (Group IV).</td><td>The filtrate is concentrated to about 15 ml. in volume. Added a little $NH_4OH$ soln. and then $Na_2HPO_4$ soln. Scratched the sides of the beaker with a glass rod. A white ppt. indicates $Mg^{++}$ (Group V).</td></tr>
</table>

*The solution should obviously be an aqueous solution. If the smaple is insoluble in water and the Group analysis is carried out with the solution in dil. HCl, tests for Group I metals may reasonably be omitted as stated earlier.

In the above table, if no ppt. is formed in any particular Group, the student should write in the respective column, "No ppt. and hence, the metal ion(s) of that Group is (or are) absent".

**Treatment of Precipitates** (*residues*) **obtained in different Groups and the confirmatory Tests.**—The students are advised to consult the reactions of individual metal ions given earlier.

**Group I ppt.**—A white crystalline ppt. of $PbCl_2$. The ppt. is soluble on boiling with water, but it reappears on cooling. The ppt. is boiled with much water and the hot soln. is used for the following confirmatory tests :

(*a*) Added potassium chromate ($K_2CrO_4$) soln. to about 2—3 ml of the hot soln. A yellow ppt. is obtained. The ppt. ($PbCrO_4$) is insoluble in acetic acid and $NH_4OH$, but soluble in alkali solns. and in $HNO_3$.

(*b*) Added KI soln. to about 2—3 ml. of the hot soln. A yellow ppt. ($PbI_2$) is obtained on cooling. The ppt. is moderately soluble in boiling water to give a colourless soln., which on cooling deposits golden yellow *spangles* (plates).

(*c*) Passed $H_2S$ gas to the hot soln. acidified with dil. HCl. A black ppt. (PbS) is formed. The ppt. issoluble on boiling with dil. $HNO_3$, glving a colourless solution.

**Group II ppt.**—The black ppt. maybe a mixture of PbS and CuS, or either of the two. The ppt. is dissolved in hot, dil. $HNO_3$ and the soln. filtered. If the soln. is perfectly colourless, $Cu^{++}$ may be taken to be absent. If it is slightly coloured (blue), either $Cu^{++}$ or both $Cu^{++}$ and $Pb^{++}$ may be present. Carry out the following confirmatory tests with the solution :

(*a*) Added $NH_4OH$ soln. to 2—3 ml. of the soln. taken in a test tube. An initial light blue ppt., followed by a deep blue colour confirms $Cu^{++}$.

(*b*) Added potassium ferrocyanide, $[K_4Fe(CN)_6]$, soln. to a small quantity of the soln. A chocolate-brown ppt. confirms $Cu^{++}$.

(*c*) Added a few drops of dil. $H_2SO_4$ to the soln., followed by the addition of about 3 ml. of alcohol. A white ppt., insoluble in dil. $HNO_3$, but soluble in ammonium acetate soln., confirms $Pb^{++}$.

(*d*) Added 1 ml. of $K_2CrO_4$ soln. to 2—3 ml. of the soln. A yellow ppt., insoluble in accetic acid, but soluble in dil. $HNO_3$, confirms $Pb^{++}$.

It may be noted that, as the two ions do not interfere with each other in the above confirmatory tests, their separation is not necessary.

**Group IIIA ppt.**—If the ppt. is white (gelatinous), it is due to $Al(OH)_3$, and $Fe^{+++}$ may be taken to be absent. But if the ppt. is reddish brown (gelatinous), either $Fe^{+++}$ alone or both $Fe^{+++}$ and $Al^{+++}$ may be present.

If the ppt. is white, dissolve it in dil. HCl and carry out the following tests with the solution to confirm $Al^{+++}$.

(*a*) To about 5ml. of the soln.. added $NH_4OH$ soln. and a little solid $NH_4Cl$. A white gelatinous ppt. is formed. The ppt. is insoluble in excess of $NH_4OH$ soln.

(*b*) To about 2—3 ml. of the soln., added NaOH soln. A white gelatinous ppt. is formed. Added excess of NaOH soln. The ppt. dissolves. Now, boiled this solution with a little (0·5 gms.) solid $NH_4Cl$. The gelatinous ppt. is again formed.

If the ppt. of Group III A is reddish brown in colour, it may contain, as stated above, only $Fe^{+++}$ or both $Fe^{+++}$ and $Al^{+++}$. In thiscase, the separation of thetwo ions arenecessary. Separation of $Fe^{+++}$ from $Al^{+++}$ is done as follows :

The reddish brown ppt. is suspended in a little water in a beaker and excess of NaOH soln. is added to it. The mixture is boiled and filtered hot. Any $Al(OH)_3$ present in the reddish brown ppt. dissolves as sodium aluminate and passes into the filtrate ; the ppt. of $Fe(OH)_3$ is not affected. The ppt. and the filtrate are tested separately for confirming $Fe^{+++}$ and $Al^{+++}$ respectively.

(I) The residue is dissolved in dil. HCl.

(*a*) To a small portion of the soln., added Potassium ferrocyanide soln. A deep blue ppt. (or colour) confirms $Fe^{+++}$.

(*b*) To a small portion of the soln., added ammonium thiocyanate soln. A deep red colour confirms $Fe^{+++}$.

(II) The filtrate is acidified with dil. HCl, and $NH_4OH$ soln. is added till alkaline. A white gelatinous ppt. confirms $Al^{+++}$.

Aluminium may also be confirmed by carrying out the *Thenard's blue* test with the white gelatinous ppt. of $Al(OH)_3$. [*See Charcoal-block test* under the **Dry** tests of basic radicals]

**Group III B ppt**.—The white ppt. is of ZnS. It may be confirmed as follows:

Dissolved the ppt. in dil. HCl and boiled off $H_2S$ completely (tested with lead acetate paper).

(*a*) The soln. is made ammoniacal and $H_2S$ gas is passed. A white ppt. of ZnS is formed. The ppt. may be filtered and $Zn^{++}$ may be confirmed by carrying out the *Rinmann's green* test with the residue. [ See *Charcoal-block test* under **Dry tests** of basic radicals.]

(*b*) Added NaOH soln. to a small portion of the above soln. A white ppt. is formed, which dissolves to give a clear solution on adding excess of NaOH soln.

**Group IV ppt.**—The white ppt. is of $CaCO_3$. Calcium may be confirmed by carrying out the **Flame test** with the ppt. It may also be confirmed as follows:

Dissolved the ppt. in dil. HCl. The soln. is made ammoniacal with dii. $NH_4OH$ soln. and then ammonium oxalate soln is added to it. A white crystalline ppt. confirms $Ca^{++}$.

**Group V ppt.**—The white ppt. is $Mg(NH_4)PO_4$. The confirmation of the metal on may be done by performing the *Charcoal block – cobalt nitrate* test, when a pink colour is obtained [ See *cobalt nitrate test* under **Dry tests** of basic radicals ]

N. B. The students might have noticed that for confirming the latter three metal ions (viz $Al^{+++}$, $Ca^{++}$ and $Mg^{++}$), we have resorted to the relevant Dry tests. It is, therefore, stressed that the Dry tests are no less important in the qualitative analysis, and as such, they should be carefully and seriously performed.

## Some Model Analysis Of Unknown Salts

It is prescribed in the syllabus that the student is to detect *two* basic radicals from one sample and *one* acid radical from another sample. It is not necessary that the first sample would not contain any acid radical or the second sample would not contain any basic radical (it is not also possible), but the student is not to detect them. As only solid samples are expected to be given, the first sample may also contain only the oxides of the two metals ; but the second sample will invariably be a *salt* which will contain the positive counterpart (either a metal ion or $NH_4^+$) of the acid radical. Here we give a procedure to show how a student should carry out the analysis systematically and present his results in the answer-script.

The unknown sample in which *two* basic radicals are to be detected may contain a mixture of two ingredients one of which is soluble in water, while the other is not [*e.g.* mixtures of $PbO+CuCl_2$ ; $CuO+Pb(NO_3)_2$ ; $Fe_2O_3+Al_2(SO_4)_3$ ; $Al_2O_3+FeSO_4$ ; $ZnO+Ca(NO_3)_2$ etc.]

In such cases, it is always an advantage to separate the water-soluble part from the other and carry out the Group Analysis with the water-soluble fraction and the portion insoluble in water (by dissolving it in dil. HCl) *separately*. Although this procedure may seem to be more time-consuming, experience has shown that such analysis ultimately takes less time and give more definite results. In such an analysis, the water-soluble portion will generally contain *one* basic radical and the other portion (i.e. solution in dil. HCl) will contain *another* basic radical.

## Identification of two Basic Radicals in an Unknown Sample

### Example—1

Date of Analysis……… Sample No………

**Colour of the sample.**—Light bluish green.

**State of aggregate.**—Amorphous powder mixed with some small white crystals.

**Solubility.**—A portion of the sample is soluble in cold water, giving a colourless solution ; the bluish green residue is soluble in dil. HCl (with effervescence), giving a green coloured solution. The sample is completely soluble in dil. HCl (with effervescence, giving a clear green soln.

*Dry Tests :*

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. Heated a small quantity of the sample in a dry test tube (*Ignition test*). | Water droplets collect at the cooler upper part of the test tube and the sample becomes black on stronger heating, with some emmission of glow. | May be a hydrated salt and the sample may contain copper or iron salt along with Ca, Mg, Al or Zn salts. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 2. Carried out the *Flame Test.* | A bluish green colour of the flame is observed ; the flame looks colourless when viewed through blue glass. | May be copper salt. |
| 3. (a) Carried out *charcoal block test* in the oxidising flame. | Black mass is obtained. | May be copper salt. |
| (b) Carried out *charcoal block test* in the reducing flame. | Red scales are obtained. Brown fumes are formed by adding a drop of conc. $HNO_3$ on the red scales. | May be copper salt. |
| (c) As the residue was black, *cobalt nitrate test* was not performed. | | |
| 4. Carried out *barax-bead test* in the oxidising and reducing flames. | The bead is green when hot and blue when cold, when heated in the oxidising flame, but it is red and opaque in the reducing flame (both hot and cold). | May be copper salt. |

*Wet Tests.* The soln. of the sample in dil. HCl is taken (green soln.). The sample is completely soluble in dil. HCl and no pptn. takes place even on cooling.

<table>
<tr><td rowspan="5">Group I ($Pb^{++}$) absent.</td><td colspan="5">A small portion of the soln. is taken in a test tube, warmed and $H_2S$ gas is passed. A black ppt. is formed. This is added to the main bulk of the soln., warmed and $H_2S$ is passed till no more ppt. is formed Filtered.</td></tr>
<tr><td rowspan="4">A black ppt. Group II ($Cu^{++}$) present. The ppt. is analysed later for confirmation.</td><td colspan="4">The filtrate is boiled until free from $H_2S$, 2-3 drops of conc. $HNO_3$ is added and again boiled for a minute. Now 2 gms. of solid $NH_4Cl$ is added, followed by the addition of excess of dil. $NH_4OH$ soln.</td></tr>
<tr><td rowspan="3">No. ppt. Group IIIA ($Fe^{+++}$ or $Al^{+++}$) absent.</td><td colspan="3">Passed $H_2S$ in the soln. till no more pptn. takes place. Filtered.</td></tr>
<tr><td rowspan="2">A white ppt Group IIIB ($Zn^{++}$) present. Confirmed later.</td><td colspan="2">$H_2S$ is boiled off Added $NH_4OH$ and $(NH_4)_2CO_3$ soln.</td></tr>
<tr><td>No. ppt. Group IV ($Ca^{++}$) absent.</td><td>Added $Na_2HPO_4$ soln. No ppt, Group V ($Mg^{++}$) absent.</td></tr>
</table>

**Treatment of Group II and Group III B precipitates : confirmatory tests.**

**Group II ppt.**—The black ppt. may contain $Cu^{++}$ (as the sample was completely soluble in dil. HCl in the cold, it is most probable that $Pb^{++}$ is absent). The ppt. is dissolved by warming with dil. $HNO_3$ and filtered (from any separated sulphur). A blue soln is obtained (hence, $Cu^{++}$ must be present). (i) To a small quantity of the soln., taken in a test tube, dil. $H_2SO_4$ is added (followed by the addition of 1—2 ml. rectified spirit). No white ppt. is formed. $Pb^{++}$ absent.

(ii) To another portion of the soln., added $NH_4OH$ soln. in excess. A deep blue soln. is formed. $Cu^{++}$ present.

(iii) To a portion of the soln. is added dil. $NH_4OH$ soln. till neutralised (a pale blue colour is obtained). Acidified the soln. with acetic acid and added potassium chromate soln. No yellow ppt. of $PbCrO_4$ is formed. Hence, $Pb^{++}$ absent.

(iv) To a portion of the soln., is added postassium ferrocyanide soln. A chocolate-brown ppt. is formed. $Cu^{++}$ present.

Hence, $Cu^{++}$alone is present in the Group II ppt.

**Group IIIB ppt.** [There is only one metal (*viz.* zinc) of this group included in W. B. syllabus and hence, the white ppt. obtained in this group must be of ZnS.] The white ppt. is dissolved in dil HCl. A clear colourless soln. is obtained. The soln is boiled to drive off $H_2S$ completely (tested with lead acetate paper).

(i) A small quantity of the soln. is taken in a test tube and dil. $NH_4OH$ soln. is added to it. A white gelatinous ppt. is formed, which dissolves in excess of $NH_4OH$ soln.

(ii) To a small quantity of the soln, dil. NaOH soln. is added. A white gelatinous ppt. is formed, which dissolves in excess of NaOH soln. $H_2S$ gas is passed to this alkaline soln. A white ppt. is formed and $Zn^{++}$ is thus confirmed.

(iii) The bulk of the soln. in HCl is treated carefully with dil NaOH soln. till a white gelatinous ppt. is formed. The ppt. is filtered and washed with water. The moist ppt. is then taken in the groove of a charcoal-block and heated strongly with a blue-pipe in the oxidising flame. A yellow incandescent residue is formed in the hot, but the colour changes to white on cooling. A drop of dil. cobalt nitrate soln. is added to the hot residue and the mass is again heated in the oxidising flame by a blow-pipe. A green coloured mass (*Rinmann's green*) is formed. So, $Zn^{++}$ is confirned.

Hence, the unknown sample contains $Cu^{++}$and $Zn^{++}$ as the basic radicals. [The sample *actually* contained $CuCO_3$ and $ZnSO_4, 7H_2O$.]

### Example—2

Date of analysis...... Sample No. .. ....

**Colour of the sample.**—Reddish brown coloured amorphous powder, intermingled with a white crystalline substance.

**Solubility.**—A portion of the sample is soluble in warm water, giving a colourless soln. and a brown residue is left. The whole of the sample is soluble in dil. HCl, giving a yellow coloured soln.

*Dry Tests.*

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. Carried out the *ignition test.* | Water droplets collect at the cooler upper part of the test tube and the colour of the sample remains brown. | Hydrated salt, and may contain iron salt. |
| 2. Carried out *flame test.* | No visible colour of flame. | — |
| 3. Carried out *charcoal block test* in (i) the oxidising as well as (ii) the reducing flames. | (i) A brown mass is obtained. | May be iron salt. |
| | (ii) A black mass is obtained, which is attracted by magnet. | May be iron salt. |
| | The black mass is dissolved in dil. $HNO_3$, and potassium ferrocyanide soln. is added. A deep blue ppt. is formed. | Most probably iron salt. |
| 4. As the residue was brown, *cobalt nitrate test* was not performed. | — | — |
| 5. Carried out *borax-bead test* in the oxidising and the reducing flames. | The bead is yellow in the oxidising flame (both when hot or cold), and bottle-green in the reducing flame (both when hot or cold). | Most probably iron salt. |

*Wet Tests.*—The soln. of the sample in dil. HCl is taken.

The soln. of the sample in dil. HCl does not deposit any solid even when cooled.

<table>
<tr><td rowspan="5">Group I<br>($Pb^{++}$)<br>absent.</td><td colspan="5">A small quantity of the soln. is taken in a test tube, warmed and $H_2S$ passed No. ppt. The soln. in the test tube is discarded.</td></tr>
<tr><td rowspan="4">Group II<br>($Pb^{++}, Cu^{++}$)<br>absent</td><td colspan="4">The soln. is boiled with 2-3 drops of conc. $HNO_3$. 2 gms. of solid $NH_4Cl$ is added to the soln. and then excess of dil $NH_4OH$ soln. is added. A brown gelatinous ppt. is formed. Filtered</td></tr>
<tr><td rowspan="3">Group IIIA<br>($Fe^{+++}$ and/or $Al^{+++}$)<br>present. The ppt. is analysed later for confirmation.</td><td colspan="3">Passed $H_2S$ to the filtrate. No ppt.</td></tr>
<tr><td rowspan="2">Group IIIB<br>($Zn^{++}$)<br>absent.</td><td colspan="2">Boiled off $H_2S$. Added dil. $NH_4OH$ soln. and then $(NH_4)_2CO_3$ soln No. ppt.</td></tr>
<tr><td>Group IV<br>($Ca^{++}$)<br>absent.</td><td>Added $Na_2HPO_4$ soln. to the filtrate and scratched the sides of the vessel No ppt.<br>Group V<br>($Mg^{++}$)<br>absent.</td></tr>
</table>

**Treatment of the Group IIIA ppt.**—As there was no precipitation in any other group except group IIIA, it is most likely that this ppt. contains two basic radicals, *viz.* $Fe^{+++}$ and $Al^{+++}$.

The brown ppt. is taken in a small beaker, boiled with moderately concentrated NaOH soln and filtered. A brown residue remains and a colourless soln. (filtrate) is obtained.

The brown ppt. is dissolved in dil. HCl, when a yellow soln. is formed. The confirmatory tests for $Fe^{+++}$ are carried out with this soln., whereas the colourless filtrate obtained from the NaOH treatment is tested for $Al^{+++}$.

**Confirmatory tests for $Fe^{+++}$.** (i) To a small portion of the yellow soln. taken in a test tube, potassium ferrocyanide soln. is added. A deep blue ppt. (*Prussian blue*) confirms $Fe^{+++}$.

(ii) To a small portion of the yellow soln. taken in a test tube, potassium thiocyanate soln. is added. A deep blood-red colour is formed, which confirms $Fe^{+++}$.

**Confirmatory test for $Al^{+++}$.** —(i) A small quantity of the colourless soln. is boiled with solid $NH_4Cl$. A gelatinous white ppt. is formed. The ppt. dissolves when boiled with NaOH soln. This confirms $Al^{+++}$.

(ii) The bulk of the colourless soln. is acidified with dil. HCl soln. It is then made ammoniacal with dil. $NH_4OH$, when a white gelatinous ppt. is formed. The ppt. is filtered and the moist residue is heated on a charcoal-block in the oxidising flame with a blow-pipe. A white incandescent mass is obtained. The mass is cooled and a drop of dil. cobalt nitrate soln. is added to it and the mass is again heated in the oxidising flame with a blow-pipe. A blue mass (*Thenard's blue*) is obtained. This confirms $Al^{+++}$.

So, the unknown sample contains $Fe^{+++}$ and $Al^{+++}$. [The sample *actually* contained $Fe_2O_3$ and $Al_2(SO_4)_3, 18H_2O$.]

### Example—3

Date of analysis...... Sample No......

**Colour of the sample.**—Black particles intermixed with a crystalline powder.

**Solubility of the sample.**—A part of the substance is soluble in cold water, giving a colourless soln. and leaving a black residue. The black residue is soluble in dil. HCl on warming, giving a green-coloured solution. The sample is completely soluble on warming with dil. HCl, giving a green-coloured soln., from which white needle-shaped crystals separate on cooling.

*Dry Tests.*

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. Carried out *Ignition test* (heating in a dry test tube). | Brown fumes are evolved. The residue obtained is a black mass, intermingled with yellow specks. | May be $Pb^{++}$ and a nitrate of heavy metal. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 2. Carried out *Flame test.* | A greenish blue colour of the flame is obtained. | May be $Cu^{++}$. |
| 3. Carried out *Charcoal-block test* in oxidising flame. | An yellow incrustation, surrounding a black mass is obtained. | May be $Pb^{++}$. |
| 4. Carried out *Charcoal-block test* in the reducing flame. | A silvery bead and red coloured scales are formed. The mass is not attracted by magnet. | May be $Pb^{++}$ and $Cu^{++}$. |
| 4. (a) The silvery bead and the red scales obtained above are dissolved in dil $HNO_3$ and filtered. The filtrate is divided into two parts. | | |
| (i) To one part, dil. $NH_4OH$ soln. is added. | (i) Deep blue soln. is obtained. | Most probably $Cu^{++}$. |
| (ii) To the other part, dil. $H_2SO_4$ is added. | (ii) A white ppt. is formed. | Most probably $Pb^{++}$. |
| 5. As the residue in the charcoal-block test was black, *cobalt-nitrate test* was not performed. | — | — |
| 6. Carried out *borax-bead test* in the oxidising and reducing flames. | The bead is green when hot and blue when cold in the oxidising flame, but red and opaque in the reducing flame (both hot and cold). | Most probably $Cu^{++}$. |

*Wet tests.*

The sample is dissolved by heating with dil. HCl. A clear green soln. is formed. The soln. is cooled. A white crystalline ppt. is formed. Filtered.

<table>
<tr><td rowspan="5">Group I ($Pb^{++}$) present.</td><td colspan="5">The filtrate is warmed and passed $H_2S$ till no more ppt. is formed. A black ppt. is obtained. Filtered.</td></tr>
<tr><td rowspan="4">Group II ($Cu^{++}$ and/ or $Pb^{++}$) present. The ppt. is analysed later for confirmation</td><td colspan="4">The filtrate is boiled till free from $H_2S$, 2-3 drops of conc. $HNO_3$ are added and boiled. Then 2 gms. of soild $NH_4Cl$ are added, followed by the addition of $NH_4CH$ soln till alkaline. No ppt.</td></tr>
<tr><td rowspan="3">Group IIIA absent.</td><td colspan="3">Passed $H_2S$ into the soln. No ppt.</td></tr>
<tr><td rowspan="2">Group IIIB absent.</td><td colspan="2">$H_2S$ is boiled off. The soln. is made ammoniacal and saturated $(NH_4)_2CO_3$ soln is added. No ppt.</td></tr>
<tr><td>Group IV absent.</td><td>A soln. of $Na_2HPO_4$ is added to the filtrate. No. ppt. Group V ($Mg^{++}$) absent.</td></tr>
</table>

**Treatment of Group I and Group II precipitates : Confirmatory tests.**

**Group I ppt.**—As there is only one basic radical, viz. $Pb^{++}$, included in this Group (according to W.B. Syllabus), the ppt. (white) must be of lead chloride. The ppt. is boiled with water. A clear colourless soln. results, from which white needle-shaped crystals deposit on cooling.

(i) To hot soln. of the above ppt., added dil. $H_2SO_4$. A white ppt., insoluble in dil. HCl is obtained.

(ii) To the hot soln., potassium chromate soln. is added. A yellow ppt. ($PbCrO_4$) is obtained, which is insoluble in acetic acid but soluble in HCl.

(iii) To the hot soln., $H_2S$ gas is passed. A black ppt. (PbS) is obtained.

(iv) To the soln., potassium iodide soln. is added. A yellow ppt. ($PbI_2$) is formed. The ppt. is soluble on heating (giving almost a colourless soln.), but it re-appears as beautiful shining yellow plates (*golden spangles*) on cooling.

Hence, the ppt. of Group I contains $Pb^{++}$.

**Group II ppt.** The black ppt may contain $Pb^{++}$ and/or $Cu^{++}$. It is dissolved in dil $HNO_3$ by warming and filtered hot. A blue filtrate is obtained. Dil $H_2SO_4$ is added to the filtrate and cooled Some white crystals deposit. These are separated by filtration. The white crystals obtained on the filter paper are tested for $Pb^{++}$ by the tests enumerated for Group I ppt., by dissolving in ammonium acetate soln., and they were found to contain $Pb^{++}$. The green filtrate was divided into two parts.

(i) In one part, added dil $NH_4OH$ soln. in excess. At first a light blue ppt. is formed, which dissolved in excess of dil. $NH_4OH$ to give a deep blue solution.

(ii) To the other part added potassium ferrocyanide soln. A chocolate-brown ppt (of copper ferrocyanide) is formed. Hence, the group II ppt. contains $Pb^{++}$ and $Cu^{++}$,

The unknown sample contains $Cu^{++}$and $Pb^{++}$. [The sample *actually* contained $Pb(NO_3)_2 + CuO$.]

N B. To analyse this sample, it would have been easier to carry out the wet tests separately for the water-soluble fraction and that soluble in dil. HCl. The aqueous soln. would contain only $Pb(NO_3)_2$ and the soln. in dil HCl only $Cu^{++}$ (as $CuCl_2$).

---

## Identification of one Acid Radical in an Unknown Sample

### Example—I

**Date of analysis...** ... Sample No.......

**Colour of the sample.** – White crystals.

**Solubility of the sample.** – Soluble in water.

**Dry tests.**

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. (*a*) A small quantity of the sample is taken in a test tube and dil HCl is added to it. | Effervescence takes place and a colourless and odourless gas is evolved. | May be $CO_3^{=}$.<br>Sulphide absent. |
| (*b*) The evolved gas is passed through clear lime-water taken in a test tube. | The lime water turns milky. | May be $CO_3^{=}$. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| (*c*) The passage of the evolved gas into the turbid lime-water is continued for some time. | The milkiness of lime-water disappears. | Most probably $CO_3^{=}$. |
| 2. A small quantity of the solid sample is heated with about 1 ml. of conc. $H_2SO_4$ and a few pieces of Cu-turnings, and again with conc. $H_2SO_4$ and $MnO_2$. | No brown or greenish-yellow gas with pungent smell is evolved. Only the colourless gas as in expt. no. 1 is evolved more briskly. | $NO_3^-$ or $Cl^-$ absent. |

**Wet tests.**

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. To about 3 ml of the aqueous soln. of the sample, $BaCl_2$ soln. is added. | A white ppt. is formed, which dissolves in dil. HCl with the evolution of a colourless and odourless gas. | $CO_3^{=}$ present. $SO_4^{=}$ and sulphide absent. |
| 2. To 3 ml. of the aqueous soln. of the sample, added $AgNO_3$ soln., followed by acidification with dil. $HNO_3$. | A white ppt. is formed, which dissolves with effervescence when dil. $HNO_3$ is added. | $Cl^-$ absent ; $CO_2^{=}$ present. |
| 3. Carried out *Ring test.* | No brown ring is formed. | $NO_3^-$ absent. |

Hence, the given sample contains carbonate ($CO_3^{=}$) radical.

### Example—2

Date of analysis ... ... Sample No..... ..

**Colour of the sample.** – Greenish blue crystals.

**Solubility of the sample.** – Soluble in water to give a bluish green soln.

**Dry tests.**

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. Added dil. HCl to the sample. | No effervescence or evolution of any gas. | $CO_3^{=}$ and $S^{=}$ absent. |
| 2. Heated the sample with conc. $H_2SO_4$. | No brown or white fumes are formed. | $NO_3^-$ and $Cl^-$ absent, |
| 3. Heated the sample with conc. $H_2SO_4$ and Cu-turnings. | No brown fumes. | $NO_3^-$ absent. |
| 4. Heated the sample with conc. $H_2SO_4$ and $MnO_2$. | No greenish yellow gas with pungent odour is evolved. | $Cl^-$ absent. |
| 5. A little of the solid sample is mixed with 3 times its bulk of anhydrous $Na_2CO_3$ and heated on a charcoal-block with the reducing blow-pipe flame. The mass is cooled and extracted with water. To the filtered extract, sodium nitroprusside soln. is added. | A violet colour is formed. | May be $SO_4^{=}$. |

**Wet Tests.**

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. Added $AgNO_3$ soln. to the aqueous soln. of the sample. | No ppt. is formed. | $Cl^-$, $CO_3^=$, $S^=$ are absent. |
| 2. Added $BaCl_2$ soln. to the aqueous soln. of the sample. | A heavy crystalline white ppt. is formed. The ppt. is insoluble in HCl and alkali. | $SO_4^=$ present. |
| 3. Carried out *Ring test* with the aqueous soln. of the sample. | No brown ring is formed. | $NO_3^-$ absent. |

Hence, the given sample contains Sulphate ($SO_4^=$) as the acid radical.

### Example—3

Date of analysis...... Sample No......

**Colour of the sample.**—White.

**Solubility of the sample.**—Insoluble in water, but soluble in dil. HCl with the evolution of a colourless gas, with smell of rotten eggs.

*Dry Tests.*

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. (*a*) Dil. HCl is added to a small portion of the sample. | A colourless gas, with smell of rotten eggs, is evolved | May be sulphide. |
| (*b*) A filter paper moistened with lead acetate soln. is held in the evolved gas. | The paper turns black. | Most probably $S^=$. |

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 2. A small quantity of the solid sample is heated with conc. $H_2SO_4$. | No brown or white fumes are evolved. Only the foul-smelling gas is evolved more briskly. | $NO_3^-$ and $Cl^-$ absent. |
| 3. A small quantity of the solid sample is heated separately with conc. $H_2SO_4$+Cu-turnings and with conc. $H_2SO_4+MnO_2$. | No evolution of brown or greenish yellow gas. | $NO_3^-$ and $Cl^-$ absent. |

*Wet Tests.*

| *Experiments* | *Observations* | *Inferences* |
|---|---|---|
| 1. Added $BaCl_2$ soln. to the soln. of the sample in dil. HCl. | No ppt. is formed. | Sulphate absent. |
| 2. Carried out *Ring test* with the soln. of the sample in dil. HCl. | No brown ring is formed. | Nitrate absent. |
| 3. As the soln. was made in dil. HCl, no test for $Cl^-$ with $AgNO_3$ soln. was done. | — | — |

4. About 0·5 gms. of the solid sample was gently boiled with 2 gms. of pure $Na_2CO_3$ and 20 ml. water in a small beaker for about 15 minutes. It was then filtered. To the cold filtrate, added sodium nitroprusside soln. A violet colour is formed. Hence, sulphide is present (*confirmed*).

The sample contains sulphide ($S^=$) as the acid radical.

## ORAL QUESTIONS

1. What are the differences between qualitative and quantitative analysis ?

2. What is meant by the *dry tests* and the *wet tests* in qualitative inorganic analysis ?

3. Why conc. HCl is used in *flame tests*? Can you suggest a method of testing barium in $BaSO_4$ by the flame test ?

4. What is *barax bead* ? Why colourless salts are not generally subjected to the *borax bead tests* ? Why the bead is to be heated separately in the oxidising and the reducing flames ? State what happens chemically in the *borax bead test.* Why a very small amount of the sample is used in the *borax bead test* ? Is it possible to carry out the test with a solution of a salt ?

5. Why is sodium carbonate used in the *charcoal block reduction test* ? Can the tests be done by heating in iron-block having a suitable cavity ? Give reasons.

6. What are the principle of separating the metal ions in different groups in the Group Analysis ?

7. Why is $Pb^{++}$ precipitated both in Group I and Group II? A sample contains both $Pb^{++}$ and $Cu^{++}$. Can you suggest a method for confirming their presence without separating them?

8. Metallic ions of Group II are precipitated by $H_2S$ from a solution acidified with HCl. What would happen if the acidification is done with $HNO_3$ ?

9. Why is $H_2S$ removed from the solution while proceeding to Group III in Group Analysis ? Why is solid $NH_4Cl$ is added ?

10. What is *Prussian blue* ? How is it formed in the detection of $Fe^{+++}$ ? How would you distinguish betwesn $Fe^{++}$ and $Fe^{+++}$ in qualitative analysis ?

11. Both $Cu^{++}$ and $Zn^{++}$ are precipitated as sulphides in the Group Analysis. Why then $Zn^{++}$ is not precipitated in Group II ?

12. $MgCO_3$ is insoluble in ammoniacal medium. Why $Mg^{++}$ is not precipitated in Group IV along with $Ca^{++}$ ?

13. Why there cannot be a wet test for $CO_3^{=}$ in a carbonate sample which is insoluble in water but soluble in acid ? Can you suggest a test for the sulphate ion in $BaSO_4$ (insoluble in water and acids) ?

14. Why a purple colour is formed when an alkaline solution of a sulphide is treated with an aqueous solution of sodium nitroprusside ?

# PREPARATION OF RACK REAGENTS

*(Distilled water should always be used)*

| NAME | APPROXIMATE STRENGTH | PREPARATION |
|---|---|---|
| 1. Hydrochloric Acid. | 5N | 420 ml. of conc. acid to be diluted to 1 litre with water. |
| 2. Sulphuric Acid. | 5N | 140 ml. of conc. acid to be diluted to 1 litre with water. |
| 3. Nitric Acid. | 5N | 310 ml. of the conc. acid to be diluted to 1 litre with water. |
| 4. Acetic Acid. | 5N | 285 ml. of the conc. (Glacial) acid to be diluted to 1 litre with water. |

[The conc. acid should be added to water with stirring.]

| NAME | APPROXIMATE STRENGTH | PREPARATION |
|---|---|---|
| 5. Ammonia solution. | 5N | 335 ml. liquor ammonia to be diluted to 1 litre with water. |

[While opening a bottle of liquor ammonia, it should be cooled first and then opened carefully.]

| NAME | APPROXIMATE STRENGTH | PREPARATION |
|---|---|---|
| 6. Caustic soda solution | 5N | 220 gms. of solid caustic soda to be dissolved in 1 litre water. |
| 7. Sodium Phosphate | N | 120 gms. of $Na_2HPO_4$, $12H_2O$ to be dissolved in 1 litre water. |
| 8. Barium chloride solution. | $\frac{N}{2}$ | 61 gms. of $BaCl_2$, $2H_2O$ crystals to be dissolved in 1 litre water. |
| 9. Calcium chloride solution. | $\frac{N}{2}$ | 55 gms. of $CaCl_2$, $6H_2O$ crystals to be dissolved in 1 litre water. |
| 10. Ammonium oxalate solution. | $\frac{N}{2}$ | 35 gms. of $[COONH_4]_2$, $H_2O$ crystals to be dissolved in 1 litre water. |
| 11. Potassium chromate solution. | $\frac{N}{2}$ | 36·5 gms. of $K_2CrO_4$ crystals to be dissolved in 1 litre water. |
| 12. Potassium ferrocyanide solution. | $\frac{N}{2}$ | 49 gms. $K_4[Fe(CN)_6]$ crystals to be dissolved in 1 litre water. |
| 13. Cobalt nitrate solution. | 3N | 44 gms. of $Co(NO_3)_2$, $6H_2O$ crystals to be dissolved in 1 litre water. |

| NAME | APPROXIMATE STRENGTH | PREPARATION |
|---|---|---|
| 14. Silver nitrate solution. | $\frac{N}{2}$ | 17 gms. of $AgNO_3$ crystals to be dissolved in 1 litre water. |
| [The solution of silver nitrate should be kept in brown bottles or kept covered by black paper]. | | |
| 15. Ammonium carbonate solution. | 4N | 160 gms. solid salt to be dissolved in a mixture of 140 ml. of liquor ammonia and 860 ml. of distilled water. |
| 15. Yellow ammonium sulphide—$(NH_4)_2S_x$ : | | $H_2S$ is to be passed through 200 ml. of liquor ammonia till the latter gets saturated, while the solution is cooled by keeping the vessel in cold water. To the saturated solution, thus prepared, are added 10 gms. of powdered flower of sulphur and 200 ml. more of liquor ammonia. The mixture is shaken well to dissolve all the sulphur and then diluted with water to 1 litre. |
| 16. Potassium permanganate solution. | 0·3N | 10 gms. of $KMnO_4$ to be dissolved in 1 litre water. |
| 17. Potassium dichromate solution. | N | 49 gms. of $K_2Cr_2O_7$ crystals to be dissolved in 1 litre water. |
| 18. Stannous chloride solution. | N | 115 gms. of $SnCl_2, 2H_2O$ crystals (or 59 gms. of pure metallic Sn) to be dissolved in 170 ml. of conc. HCl ; the resulting solution is diluted with water to 1 litre and kept in a bottle containing a strip of pure Sn. |
| 19. Iodine solution | N | 12·7 gms. of crystalline iodine to be dissolved in a solution of 20 gms. of pure KI in 30 ml. water, and the resulting solution to be diluted to 1 litre with water. |
| 20. Ammonium chloride solution. | 2N | 105 gms of $NH_4Cl$ to be dissolved in 1 litre water. |

| NAME | APPROXIMATE STRENGTH | PREPARATION |
|---|---|---|
| 21. Ferric chloride solution. | N | 90 gms. of $FeCl_3, 6H_2O$ to be dissolved in 1 litre of water containing 20 ml. of conc. HCl. |
| 22. Copper sulphate solution. | N | 125 gms. of $CuSO_4, 5H_2O$ crystals to be dissolved in 1 litre water. |
| 23. Ferrous sulphate solution. | $\frac{N}{2}$ | 140 gms. of $FeSO_4, 7H_2O$ crystals to be dissolved in 1 litre of water containing 7 ml. of conc. $H_2SO_4$. |

[N.B. As ferrous salts are readily oxidised by aerial oxygen to ferric state, it is advisable to use always a freshly prepared solution of ferrous sulphate. To do this, the crystals of ferrous sulphate are to be washed first with a little water to remove any superficial ferric sulphate formed, dried by soaking with filter paper, weighed and then dissolved in water.]

| NAME | APPROXIMATE STRENGTH | PREPARATION |
|---|---|---|
| 24. Lead acetate solution. | N | 190 gms. of $Pb(CH_3COO)_2, 3H_2O$ crystals to be dissolved in 1 litre of water containing 10 ml. of glacial acetic acid. |
| 25. Potassium thiocyanate solution. | N | 97 gms. of KCNS crystals to be dissolved in 1 litre water. |
| 26. Sodium thiosulphate solution. | $\frac{N}{10}$ | 23 gms. of $Na_2S_2O_3, 5H_2O$ crystals to be dissolved in 1 litre of water. |
| 27. $SO_2$-solution (saturated). [or. $SO_2$-water (saturated)]. | 0·33N | To be prepared by saturating a certain quantity of water by passing $SO_2$ at ordinary temperature. |
| 28. Chlorine-water (saturated). | 0·2N | To be prepared by saturating a certain quantity of water by passing chlorine gas at ordinary temperature. |
| 29. Bromine-water (saturated). | 0·5N | 10 ml. Bromine (liquid) to be added to 1 litre of water and shaken well [A little bromine is to be kept in excess (undissolved) at the bottom.] |

[N.B. Bromine is highly corrosive and hence, it should be handled very carefully.]

| NAME | APPROXIMATE STRENGTH | PREPARATION |
|---|---|---|
| 30. (*a*) Fehling's solution—No. 1. | | 66·28 gms. of $CuSO_4,5H_2O$ crystals to be dissolved in 1 litre of water. |
| (*b*) Fehling's solution—No. 2. | | 350 gms. of Rochelle salt to be dissolved in 1 litre of water, containing 140 gms. of NaOH. |
| 31. Sodium nitroprusside solution. | | To be prepared freshly, when required, by dissolving a few crystals in a little water. |
| 32. Fusion mixture. | | 106 gms. of $Na_2CO_3$ are to be mixed intimately with 140 gms. of $K_2CO_3$. |
| 33. Dimethyl glyoxime | 1% | Dissolve 1 gm. of the solid substance in 100 ml. of rectified spirit. |

**Indicators.**

(1) **Litmus solution.**—100 gms. of Litmus grains are to be digested with 500ml. hot water. The mixture is allowed to c over-night and filtered. The filtrate is mixed with 300 ml. of rectified spirit and the mixture is kept again over-night. It is then filtered and the filtrate is diluted to 1 litre with water.

(2) **Phenolphthalein.**—5 gms. Phenolphthalein are to be dissolved in 100 ml. of warm rectified spirit and the solution is diluted to 1 litre with equal volumes of water and rectified spirit.

(3) **Methyl orange.**—2 gms. of solid Methyl orange are to be dissolved in 200 ml. rectified spirit and the solution is then diluted to 1 litre with water.

## TABLE OF SOLUBILITIES

| | $Ag^+$ | $Hg_2^{+2}$ | $Pb^{+2}$ | $Hg^{+2}$ | $Bi^{+3}$ | $Cu^{+2}$ | $Cd^{+2}$ | $As^{+3}$ | $Sb^{+3}$ | $Sn^{+2}$ | $Sn^{+4}$ | $Fe^{+2}$ | $Fe^{+3}$ | $Cr^{+3}$ | $Al^{+3}$ | $Co^{+2}$ | $Ni^{+2}$ | $Mn^{+2}$ | $Zn^{+2}$ | $Ba^{+2}$ | $Sr^{+2}$ | $Ca^{+2}$ | $Mg^{+2}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Oxide or $OH^-$ | DN* | DN | DN | DH | CH | DH | DH | DH | DH | DH | In. | DH† | DH | DH‡ | DH‡ | CH | MH | CH | DH | W | W<br>(DH) | W<br>(DH) | DH |
| $CO_3^=$ | DN | DN | DN | DH | DH | DH | DH | — | — | — | — | DH | — | — | — | DH | DH | DH | DH | DH | DH | DH | DH |
| $S^=$ | DN | — | DN | AR | DN | DN | DH | CN | CH | CH | CH | DH | — | — | — | CN | CN | DH | DH | DH | DH | DH | DH |
| $F^-$ | W | DN | DN | DN | DH | DH | W | — | W | W | W | W | W | DH | W | W | DH | DH | W | DH | DH | In. | DH |
| $Cl^-$ | In.* | CN | HW | W | DH | W | W | W | DH | W | W | W | W | W | W | W | W | W | W | W | W | W | W |
| $Br^-$ | In. | CN | HW | W | DH | W | W | — | DH | W | W | W | W | W | W | W | W | W | W | W | W | W | W |
| $I^-$ | In. | CN | HW | CN | DH | — | W | — | DH | W | DH | W | — | — | W | W | W | W | W | W | W | W | W |
| $BO_3^{-3}$ | DN | DN | DN | DH | DH | DH | DH | — | — | DH | — | DH | DH | DH | DH | DH | DH | DH | DH | DH | DH | DH | DH |
| $PO_4^{-3}$ | DN | DN | DN | DH | DH | DH | DH | — | — | DH | CH | DH | DH | DH | DH | DH | DH | DH | DH | DH | DH | DH | DH |
| $AsO_3^{-3}$ | DN | DN | DN | DH | — | DH | — | — | — | DH | — | DH | DH | W | — | DH | DH | DH | DH | DH | DH | DH | DH |
| $AsO_4^{-3}$ | DN | DN | DN | DH | DH | DH | DH | — | — | DH | CH | DH | DH | DH | DH | DH | DH | DH | DH | DH | DH | DH | DH |
| $CrO_4^=$ | DN | DN | DN | DH | DH | DH | DH | — | — | — | — | DH | DH | — | DH | DH | DH | DH | DH | DH | W | W | W |
| $SO_4^=$ | W | DN | In. | DH | W | W | W | — | — | W | — | W | W | W | W | W | W | W | W | In. | In. | W(CH) | W |

Abbreviations : W=Water ; HW=Hot water ; W(DH)=Soluble in water, better in dilute HCl ; W(CH)=Soluble in water, better in conc. HCl ; DH=Dilute HCl ; CH=conc. HCl , MH=Medium conc. HCl ; DN=Dilute $HNO_3$ ; CN=conc. $HNO_3$ ; In.—Insoluble ; AR=Aqua regia ; * $Ag_2O$, $Ag(OH)$ and AgCl are soluble in ammonium hydroxide ; †=Ignited ferric oxides is insoluble, only partially soluble in hot conc. HCl. ‡ Freshly precipitated hydroxides (or hydrated oxide) of $Al^{+3}$ or $Cr^{+3}$ are soluble in dilute HCl, but ignited $Al_2O_3$ and also $Cr_2O_3$ are insoluble.

Notes : (1) Salts of $Na^+$, $K^+$ and $NH_4^+$ are soluble in water. (2) All nitrates and nitrites, except certain basic nitrates and silver nitrite, are soluble in water.

## TABLE 1. PRESSURE OF WATER VAPOUR (AQUEOUS TENSION) IN MILLIMETRES OF MERCURY

| *Temp.* (°*C*) | *Pressure* (*mm.*) | *Temp.* (°*C*) | *Pressure* (*mm*) | *Temp.* (°*C*) | *Pressure* (*mm.*) | *Temp.* (°*C*) | *Pressure* (*mm.*) |
|---|---|---|---|---|---|---|---|
| 0·0 | 4·6 | 15·5 | 13·1 | 22·0 | 19·7 | 28·0 | 28·1 |
| 5·0 | 6·5 | 16·0 | 13·5 | 22·5 | 20·3 | 28·5 | 28·9 |
| 10·0 | 9·2 | 16·5 | 14·0 | 23·0 | 20·9 | 29·0 | 29·8 |
| 10·5 | 9·5 | 17·0 | 14·4 | 23·5 | 21·5 | 29·5 | 30·7 |
| 11·0 | 9·8 | 17·5 | 14·9 | 24·0 | 22·1 | 30·0 | 31·6 |
| 11·5 | 10·1 | 18·0 | 15·4 | 24·5 | 22·8 | 40·0 | 54·9 |
| 12·0 | 10·5 | 18·5 | 15·9 | 25·0 | 23·5 | 50·0 | 92·1 |
| 12·5 | 10·8 | 19·0 | 16·4 | 25·5 | 24·2 | 60·0 | 149·2 |
| 13·0 | 11·2 | 19·5 | 16·9 | 26·0 | 25·0 | 70·0 | 233·8 |
| 13·5 | 11·5 | 20·0 | 17·4 | 26·5 | 25·7 | 80·0 | 355·4 |
| 14·0 | 11·9 | 20·5 | 17·9 | 27·0 | 26·5 | 90·0 | 526·0 |
| 14·5 | 12·3 | 21·0 | 18·5 | 27·5 | 27·3 | 100·0 | 760·0 |
| 15·0 | 12·7 | 21·5 | 19·1 | | | | |

## TABLE 2. DATA ON THE STRENGTH OF COMMON ACIDS AND LIQUOR AMMONIA.

| *Name* | *Approximate* | | | *Vol. required to make 1 litre of approx.* (*N*) *solution* (*ml.*) |
|---|---|---|---|---|
| | *Per cent by weight* | *Specific gravity* | *Normality* (*N*) | |
| **Hydrochloric Acid** | 35 | 1·18 | 11·3 | 89 |
| **Nitric Acid** | 70 | 1·42 | 16·0 | 63 |
| **Sulphuric Acid** | 96 | 1·84 | 36·0 | 28 |
| **Phosphoric Acid** | 85 | 1·69 | 41·1 | 23 |
| **Acetic Acid** | 99·5 | 1·05 | 17·4 | 58 |
| **Liquor Ammonia** | $27(NH_3)$ | 0·90 | 14·3 | 71 |

## TABLE OF ATOMIC WEIGHTS (based on carbon 12=12·0000)

| Element | Symbol | Atomic Number | Atomic Weight | Element | Symbol | Atomic Number | Atomic Weight |
|---|---|---|---|---|---|---|---|
| Actinium | Ac | 89 | 227 | Mercury | Hg | 80 | 200.59 |
| Aluminium | Al | 13 | 26.98 | Molybdenum | Mo | 42 | 95.94 |
| Americium | Am | 95 | (243) | Neodymium | Nd | 60 | 144.24 |
| Antimony | Sb | 51 | 121.77 | Neon | Ne | 10 | 20.183 |
| Argon | Ar | 18 | 39.946 | Neptunium | Np | 93 | (237)* |
| Arsenic | As | 33 | 74.92 | Nickel | Ni | 28 | 58.71 |
| Astatine | At | 85 | (210)* | Nobium | Nb | 41 | 92.91 |
| Barium | Ba | 56 | 137.34 | Nitrogen | N | 7 | 14.007 |
| Berkelium | Bk | 97 | (249)* | Nobelium | No | 102 | (253)* |
| Beryllium | Be | 4 | 9.012 | Osmium | Os | 76 | 190.2 |
| Bismuth | Bi | 83 | 208.98 | Oxygen | O | 8 | 15.99943 |
| Boron | B | 5 | 10.81 | Palladium | Pd | 46 | 106.4 |
| Bromine | Br | 35 | 79.909 | Phosphorus | P | 15 | 30.974 |
| Cadmium | Cd | 48 | 112.40 | Platinum | Pt | 78 | 195.09 |
| Calcium | Ca | 20 | 40.08 | Plutonium | Pu | 94 | (242)* |
| Californium | Cf | 98 | (251)* | Polonium | Po | 84 | 210 |
| Carbon | C | 6 | 12.01115 | Potassium | K | 19 | 39.102 |
| Cerium | Ce | 58 | 140.12 | Praseodymium | Pr | 59 | 140.907 |
| Caesium | Cs | 55 | 132.91 | Promethium | Pm | 61 | (147)* |
| Chlorine | Cl | 17 | 35.453 | Protoactinium | Pa | 91 | (231)* |
| Chromium | Cr | 24 | 52.00 | Radium | Ra | 88 | 226.05 |
| Cobalt | Co | 27 | 58.933 | Radon | Rn | 86 | 222 |
| Copper | Cu | 29 | 63.54 | Rhenium | Re | 75 | 186.23 |
| Curium | Cm | 96 | (247)* | Rhodium | Rh | 45 | 102.92 |
| Dysprosium | Dy | 66 | 162.50 | Rubidium | Rb | 37 | 85.47 |
| Einsteinium | Es | 99 | (254) | Ruthenium | Ru | 44 | 101.07 |
| Eribium | Er | 68 | 167.26 | Samarium | Sm | 62 | 150.35 |
| Europium | Eu | 63 | 152.0 | Scandium | Sc | 21 | 44.956 |
| Fermium | Fm | 100 | (253)* | Selenium | Se | 34 | 78.96 |
| Fluorine | F | 9 | 19.00 | Silicon | Si | 14 | 28.086 |
| Francium | Fr | 87 | (223)* | Silver | Ag | 47 | 107.87 |
| Gadolinium | Gd | 64 | 157.25 | Sodium | Na | 11 | 22.9898 |
| Gallium | Ga | 31 | 69.72 | Strontium | Sr | 38 | 87.62 |
| Germanium | Ge | 32 | 72.59 | Sulphur | S | 16 | 32.064 |
| Gold | Au | 79 | 196.97 | Tantalum | Ta | 73 | 180.948 |
| Hafnium | Hf | 72 | 178.49 | Technetium | Tc | 43 | (99)* |
| Helium | He | 2 | 4.003 | Tellurium | Te | 52 | 127.60 |
| Holmium | Ho | 67 | 164.93 | Tebium | Tb | 65 | 158.94 |
| Hydrogen | H | 1 | 1.007967 | Thallium | Tl | 81 | 204.37 |
| Indium | In | 49 | 114.82 | Thorium | Th | 90 | 232.038 |
| Iodine | I | 53 | 126.90 | Thulium | Tm | 69 | 168.934 |
| Iridium | Ir | 77 | 192.20 | Tin | Sn | 50 | 118.69 |
| Iron | Fe | 26 | 55.85 | Titanium | Ti | 22 | 49.90 |
| Krypton | Kr | 36 | 83.80 | Tungsten | W | 74 | 183.85 |
| Lanthanum | La | 57 | 138.91 | Uranium | U | 92 | 238.08 |
| Lawrencium | Lw | 103 | (257)* | Vanadium | V | 23 | 50.942 |
| Lead | Pb | 82 | 207.19 | Xenon | Xe | 54 | 131.30 |
| Lithium | Li | 3 | 6.939 | Ytterbium | Yb | 70 | 173.04 |
| Lutecium | Lu | 71 | 174.97 | Yttrium | Y | 39 | 88.905 |
| Magnesium | Mg | 12 | 24.312 | Zinc | Zn | 30 | 65.37 |
| Manganese | Mn | 25 | 54.94 | Zirconium | Zr | 40 | 91.22 |
| Mendelevium | Md | 101 | (256)* | | | | |

*Figures in the parantheses are the mass numbers of the most stable isotope known.